ANALYTICAL STUDIES OF SURFACTANTS

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

Master of Philosophy

IN

APPLIED CHEMISTRY

Submitted by

Showkat Ahmad Bhawani

Under the supervision of

Dr. ALI MOHAMMAD

DEPARTMENT OF APPLIED CHEMISTRY
FACULTY OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH U.P. (INDIA)

2006

Research is to see what everybody else has seen,
and to think what nobody else has thought.

--------- *Albert Szent Gyvrgi*

DEDICATED

To My

Loving Family

DEPARTMENT OF APPLIED CHEMISTRY

Dr. Ali Mohammad
Ph.D., D.Sc. (F.N.A.Sc.)
EDITOR : Chemical & Environmental Research

Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh-202 002, India
564-230 AMU IN (Telex) . 91-571-700920, 700921 (Tel) . 456 (Ext.) . mohammadali4u@rediffmail.com (E-mail)

CERTIFICATE

This is to certify that the work embodied in this thesis entitled "**Analytical Studies of Surfactants**" is the original contribution of **Mr. Showkat Ahmad Bhawani**, carried out under my guidance and supervision, and it is suitable for the award of degree of Master of Philosophy in Applied Chemistry from Aligarh Muslim University, Aligarh.

A. Mohammad
17/5/06

(Dr. Ali Mohammad)
Supervisor

Residence : "AL-RAIYAN" Iqra Colony, New Sir Syed Nagar, Aligarh-202002 (INDIA), ☎ : 0571-408196

Acknowledgement

When every hope is gone, and helpless flee: help comes from I know not where, this is the essence of GOD. I am thankful to Allah (SWT) sustainer of the worlds, who bestowed upon me the opportunity to accomplish this work, which would have not seen the light of the day otherwise. The Holy verses and Prophets (PBUH) sayings have always infused in me a zest to explore the unknown. I pray to Allah to advance me in knowledge and that my endeavors guide me towards the right path.

First of all, I wish to express my sincere and deep sense of gratitude to my supervisor Dr. Ali Mohammad, for expert guidance, persistent interest, scholarly criticism and constant encouragement throughout the course of this study.

I am highly obliged to Prof. H. S. Rathore, Chairman, Department of Applied Chemistry, Aligarh Muslim University, Aligarh for providing me research facilities and kind support through out the period of endeavor to M.Phil study.

I am also thankful to my research colleagues Sufia Hina, Abdul Moheman, Hina Shahab, Ruby Gupta, Almas Zehra and Nazrul Haq whose guidance and cooperation at every stage has enabled me to complete this work successfully and efficiently.

I would like to offer my sincere thanks to all my friends/seniors particularly Dr. Abu Tariq, Dr. Faisal, Dr. Yasser Azim, Shahper, Imran, Firdoos, Azhar, Yousuf, Sajjad, Mushtaq, Saquib, Saurabh, Mohammad Faisal, F. Mallah, J. Masoodi, Irshad Bhat, Adnan and Sajid for their valuable day-to-day help throughout the tenure of this work whenever needed.

I must express my thanks to all the teaching staff of the department for their kind cooperation during research.

I am also thankful to non-teaching staff of the department for their cooperation.

I am also thankful to Zaheer Ahmad, Limra Computers for carrying out important type setting of the thesis.

Finally, I don't find suitable words to express my deepest thank and gratitude to my parents, brothers, sisters, brothers in law and nephews for their love, untiring assistance, constant support and encouragement throughout the tenure of this work.

Showkat Ahmad

(Showkat Ahmad Bhawani)

CONTENTS

Page No.

CHAPTER-1 General Introduction

1.1	Introduction	1-2
1.2	Separation Techniques	2-4
1.3	Thin-layer Chromatography	4-6
1.4	TLC Procedure	6-9
1.5	Chromatographic Systems	9-11
1.6	Visualization	11
1.7	Qualitative Analysis	12-13
1.8	Quantitative Analysis	13
1.9	Advantages	13
1.10	Combination of TLC with other Analytical Techniques	14
1.11	Surfactants	15-16
1.12	Classification of Surfactants	17-21
1.13	Analytical Methods for Surfactants	21-22
1.14	Applications of Surfactants	22-26
1.15	Literature	26-115
	References	116-122

CHAPTER-2 Silica Thin-Layer Chromatographic Separation of Cetylpyridinium Chloride (CPC) from Polyoxyethylene (20) Sorbitan Monolaurate (Tween-20)

2.1	Introduction	123-124
2.2	Experimental	124-128
2.3	Results and Discussion	128-130
2.4	Application	130
	Tables and Figures	131-137
	References	138-140

Chapter - 1

General Introduction

1.1 INTRODUCTION

Analytical chemistry has extensive applications in the analysis of organic and inorganic compounds, Pharmaceuticals, bio-chemicals, body fluids, polluted water, food and many other areas. With the global awareness in health hazards and environmental pollution, analytical chemistry has played key role to unveil its causes. Modern sophisticated computerized instrumental techniques made possible to elucidate the microstructure of molecular species and to obtain substances in the highest state of purity. This branch usually begins by placing chemical analysis in the broader prospective of chemical science, describing different methods of analysis e.g. qualitative (deals with finding what constituent or constituents are in analytical sample) and quantitative (deals with the determination of how much of given substance is in the sample) on macro to micro level and can also be applied to the routine analysis. According to the type of process used to perform the analysis, methods used for chemical analysis can be categorized as given in Figure 1.1.

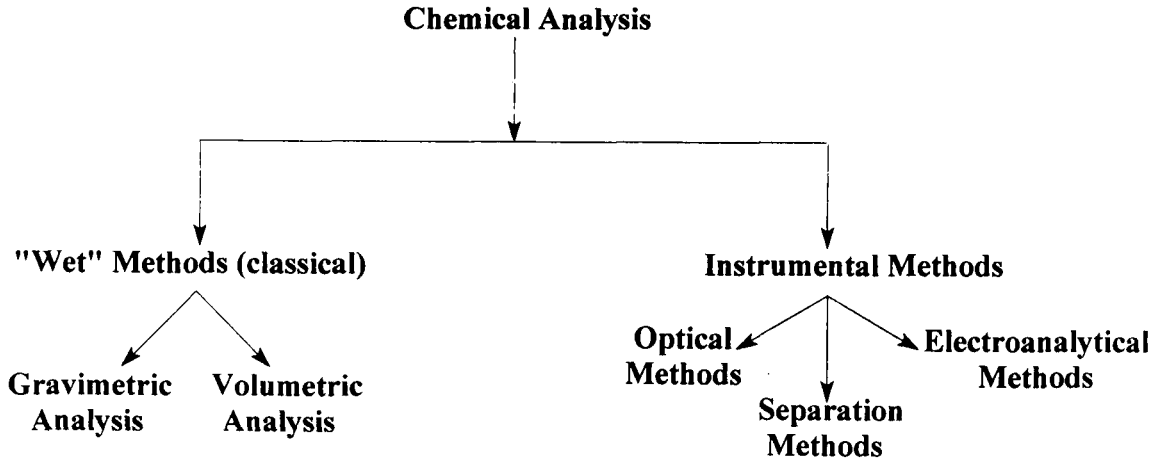


Figure 1.1: The Major Categories of Chemical Analysis

Instrumental as well as non-instrumental (or classical) methods are being employed for the analysis of air water and soil pollutants. Since instrumental analysis is becoming increasingly automatic and research oriented. Despite the advantages offered by the instrumental methods in various fields, their wide spread adoption has not rendered the classical methods obsolete for the simple reasons that firstly, they cannot be applied if the analyte is present in large concentration and secondly, it is absolutely imperative to use classical methods (volumetric or gravimetric) of analysis for standardization of newer methods. In fact classical methods deserve to be strengthened because they are simple, inexpensive and versatile.

1.2 SEPARATION TECHNIQUES

The identification and separation of various species can be achieved by an array of systematic procedures. Among the most versatile analytical separation techniques, chromatography has wider applicability.

Chromatography

In spite of the popular belief and general acceptance of the contribution of *Tswett* as being the real discoverer of chromatography (literally "color writing" from the Greek), the starting of chromatography predated to the work of *F.F. Runge* who investigated the separation of colored substances (i.e. dyes) on paper (1). The work carried out by *Goppelsroeder* (2) and *Schonbein* (3) on chromatographic separation of substances on filter paper has been included in a report published by *Fischer* and *Schmidner* (4) in 1892. However, the concept of separation on columns may be attributed to Reed's work, which was followed by Day who separated petroleum fractions with the help of columns (5, 6). The paper published in 1906 by M. Tswett, a lecturer of Botany at the University of Warsaw provided the first description in nearly modern terms of chromatographic separation (7). He described the resolution of different components of pigments as colored bands on a calcium carbonate column like spectrum of light rays and termed it as "Chromatogram". The actual importance of

Tswett's work remained dormant until about 1931, when separations of plant carotene pigments were reported by prominent organic chemist *Kuhn* (8, 9). His research attracted much attention and adsorption column chromatography became invaluable tool in the field of natural product chemistry. In 1941, *Martin* and *Synge* (10, 11) laid another milestone in development of chromatography by reporting their discovery of liquid-liquid partition chromatography. One liquid was used as adsorbent and another liquid was allowed to percolate through the former, thus making the technique as a chromatographic process. This work initialized the development of other forms of chromatography.

Chromatography is a phenomenon in which two or more compounds in a mixture are physically separated by distributing between two phases: (i) a stationary phase which can be a solid or a liquid supported on solid and (ii) a mobile phase (either a gas or a liquid) which flows continuously through the stationary phase. Differences in the affinity of individual components facilitate their separation. Chromatography is a collective term, which is applicable to all methods that appear diverse in some regards but share certain common features. The basis of several related separation methods is the differential migration from a narrow initial zone of mixture with suitable combination of driving force and resistive action of which either one or both must be selective in order to achieve effective separations. The chromatrographic systems can be classified according to (a) state of aggregation of the phases, (b) physical arrangement of the phases and (c) mechanism operating in the distribution equilibrium.

Chromatographic systems generating from solid, liquid and gaseous phases are (a) liquid-liquid (b) liquid-solid (c) gas-liquid and (d) gas-solid. If the mobile phase is a gas, the technique is known as "*Gas Chromatography*" and if it is a liquid then the technique is called "*Liquid Chromatography*". The stationary phase may be in the form of flat bed consisting of adsorbent spread uniformly on a sheet of glass or aluminium (*thin-layer chromatography*) or a sheet of cellulose (*paper chromatography*) or packed

into a glass or metal column (*column chromatography*). According to the mode of separation of mechanism, chromatography can be adsorption, partition, ion- exchange, size exclusion, electrochromatography etc. A simple classification of Chromatographic methods is summarized in Table 1.1.

Table 1.1: Classification of Chromatographic Methods

S.No.	Type of Chromatography	Examples
1.	Adsorption chromatography	Column chromatography, thin layer chromatography, gas solid chromatography
2.	Partition chromatography	Paper chromatography, reversed phase thin layer chromatography, classical liquid-liquid chromatography
3.	Modified partition (or bonded phase chromatography)	High performance liquid chromatography (HPLC) and high performance (HP) TLC
4.	Ion exchange chromatography	Cation and anion exchange chromatography
5.	Exclusion chromatography	Ion exchange and gel permeation chromatography, molecule or sieve chromatography
6.	Electrochemistry	Capillary and zone electrophoresis

Since the work presented in this thesis is mainly based on the use of thin layer chromatography as an analytical tool, it is necessary to mention the salient features of this technique. The following paragraphs are devoted to cover all-important aspects of the development and current state-of-art procedure of thin-layer chromatography.

1.3 THIN-LAYER CHROMATOGRAPHY

Thin-layer chromatography (TLC) a subdivision of liquid chromatography is carried out on a flat surface and hence it is sometimes referred to as *planar chromatographic separation technique.* In TLC, the

mobile phase (a liquid) migrates through the stationary phase (thin layer of porous sorbent on a flat inert surface) by capillary action. This technique is simple, versatile and inexpensive for separating and identifying the components of complex mixtures of inorganic, organic and biochemical substances.

The beginning of TLC can be ascribed to the report of Dutch biologist, *Beyerink* (12), who separated hydrochloric and sulfuric acids in the form of fine rings on thin layer of gelatin using a visualizing agent. Following the same method, *Wijsman* (13) identified the presence of two enzymes in malt diastase using a fluorescent method for detecting separated enzymes on thin layer. He used the bacteria obtained from sea water as fluorescent agent. However, the invention of TLC is usually credited to two Russian Scientists; *N. A. Izmailov* and *M.S. Schraiher*, who used binder free horizontal thin layers (2 mm thick) of alumina spread on glass plate to the analysis of pharmaceutical preparations which led to the publication of their classical paper (14) on "*A Spot Chromatographic Method of Analysis and its Application in Pharmacy*" in 1938. Since their method consists of depositing a drop of sample solution being investigated and the development by the application of several drops of solvent on flat surface of adsorbent before observing the separated zones, it was called "*Drop Chromatography or Spot Chromatography*". They also pointed out the usefulness of this method for preliminary testing of sorbent properties before their utilization in the form of column. Though *Izmailov* is best known for his fundamental work on TLC, his main field of interest was electrochemistry for which he received the *Mendeleiv* Prize of the Academy of Science of USSR in 1961.

In 1939, Brown developed a useful technique called "*Circular Paper Chromatography*" which involves the placing of filter paper between two glass plates and the application of sample and the developing solvent through a small hole of the upper plate. To obtain stronger adsorbent, he proposed the use of a thin layer of alumina between two sheets of paper. In 1940, *Lapp* and *Erali* used a loose layer of alumina spread on a glass slide that was

supported on an inclined aluminium sheet. This sheet was cooled at its upper end and heated at the lower end. The sample was placed at the top of the adsorbent layer and gradually developed by solvent descending movement. The use of heat at the lower end of the layer increased the evaporation rate of the solvent so that increased development could take place (15). It is interesting that, in 1949 two American Chemists, *Meinhard* and *Hall* (16) gave the concept of "Surface Chromatography" and described their work on the use of microscope slides coated with a mixture of alumina (an adsorbent) and celite (a binder) to separate Fe^{2+} and Zn^{2+}. Their work was probably the first application of TLC for the separation of inorganic ions.

TLC is the most widely used chromatographic method because of the following reasons, (a) The availability of limited number of liquid chromatographs in research laboratories (b) simplicity of the techniques (c) possibility of simultaneous analysis of a large number of samples (d) low cost and (e) the ease of operation by a researcher with little experience. Numerous publications on TLC applications attest to the versatility and applicability of this technique in all branches of science. It has opened new fields of exploration and become an invaluable aid to separation scientists.

TLC can be used for (a) qualitative analysis (to identity the presence or absence of a particular substance in a mixture (b) quantitative analysis (to determine precisely and accurately, the amount of a particular substance in a sample mixture) and (c) preparative analysis (to purify and isolate a particular substance for subsequent use). All three cases require the common procedures of sample application, chromatographic separation and sample component visualization. However, analytical TLC differs from preparative TLC as the sample solution/or amount is applied on thinner layers in the former case, whereas thicker TLC plates are used for preparative TLC.

1.4 TLC PROCEDURE

The TLC process is an off-line process in which all the procedural steps, depicted in Figure 1.2 are carried out

independently. The basic TLC procedure involves the spotting of sample mixture (5-10 μL) at about 2 cm above the lower edge of the TLC plate, drying the spot (usually at room temperature). development of plate with suitable mobile phase to a distance of 8-10 cm inside a cylindrical or rectangular closed chamber by ascending technique, withdrawing plate from the developing chamber, drying the layer at room temperature to remove the mobile phase, detection of spots on TLC plate using suitable detection reagent, measurement of R_F values of the resolved spots and the quantitative estimation of the analyte after extraction from the layer with suitable extractant. The differential migration of components results due to varying degrees of affinity of the components in a mixture for stationary and mobile phases.

Sample Preparation: Standard methods for sample preparation identification and separation of analyte present in a variety of samples such as plants, food, biological, geological and environmental samples have been reported. In general, solutions of the surfactants are prepared by dissolving appropriate weights in methanol to give concentrations of 1% (1g / 100 ml).

TLC Plate Preparation or Coating Procedures: The contemporary trend is of using commercially available pre-coated plates. The manual preparation of layers involves the coating of slurry of the adsorbent (silica gel, alumina and keiselguhr) on glass, aluminium or plastic sheet (20x20 or 20x10cm) with the help of TLC applicator. The thickness of dried layer for analytical purposes is kept to 0.2-0.3 mm. A binder (starch, gypsum, dextrin or polyvinyl alcohol) is usually added to the layer material to provide better adhesion mechanical stability and durability.

Sample Application: Sample application is one of the most important steps in the technology of TLC. Improperly applied samples result in poor chromatograms. Sample can be applied as spot or streak using micropipette, microsyringe, melting point capillaries etc. A number of automatic spotters of varying design are available for sample application. The nanoapplicator

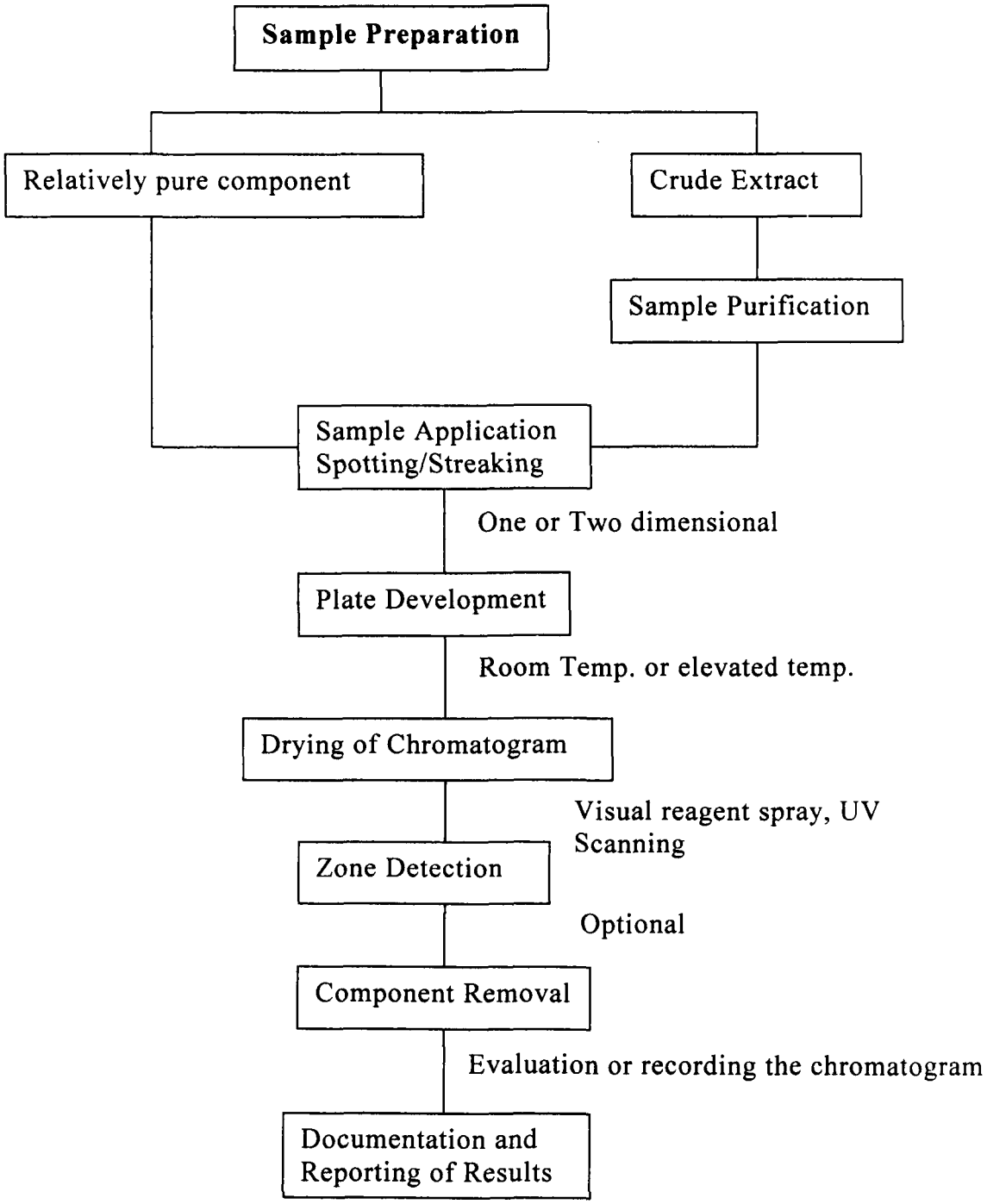


Figure 1.2: Scheme of Typical Thin-Layer Chromatographic Process

(Nanomat) is an example of micrometer controlled syringes which has a dynamic volume range of 50-230 nL. Another applicator (Linomat) allows sample application in narrow bands. The application of sample as streak or band provides more efficient separations. The sample should be completely dried before placing the plate in the developing chamber. Dilute solutions can be applied to the layer either with sorbent drying between successive applications or after bringing the sample solution to proper concentration.

Development Modes: The process of migration of mobile phase through the sorbent layer to effect separation of the sample substance is called development. Ascending development has been the most commonly used mode of development in TLC. Other development modes such as multiple, stepwise, circular two-dimensional and reversed-phase partition development have also been used to limited extent. The distance for the migration mobile phase has been kept to 10-12 cm for conventional TLC. While performing the development one should take care of the angle of the development and saturation of chamber apart from other factors.

1.5 CHROMATOGRAPHIC SYSTEMS

The stationary and mobile phases together comprise the chromatographic system. The proper selection of stationary and mobile phase conditions decides the degree to which effective separations of components in a mixture can be achieved.

Stationary Phase (Layer Sorbent): Silica gel, an amorphous and porous sorbent has been the most preferred layer material followed by alumina and cellulose. Thin layers of silica gel G (gypsum binder) and silica gel S (starch binder) with or without, "fluorescent indicator" have been used more frequently. Silica gel is slightly acidic in nature. At the surface of silica gel the free valences of the oxygen are connected either with hydrogen (Si-O-H, silanol groups) or with another silicon atom (Si-O-Si, siloxane groups). The silanol groups represent adsorption active surface centers that are able to interact with solute molecules. On the other hand, alumina (aluminium oxide)

is basic and is more reactive than silica gel. Adsorption is the separation mechanism in both silica gel and alumina. Cellulose, an organic material is used as a sorbent in TLC when it is convenient to perform a given paper chromatographic separation by TLC with decreased development time and increase in the sensitivity of detection. Mixed layers (impregnated and non-impregnated) have also been used by several workers for achieving enhanced resolution of components. Mixed layers are usually of medium activity as compared to the separated phases. The addition of kieselguhr in silica generally reduces the activity of silica, resulting in a new sorbent layer with altered activity that is capable of providing peculiar separations, not possible on separated phases. The mixed layers of upto three or four sorbents have been occasionally prepared and used for specific TLC applications. However, binary (or biphasic) sorbent layers have been more commonly used for routine analysis of organic as well as inorganic mixtures.

Mobile Phase (Solvent System): In TLC, the separation of ions is usually governed by the physical interactions of the adsorbent and the coordinative properties of the mobile phase. The mixture of organic solvents containing some aqueous acid, base or a buffer is, in general well suited for the separation of ionic species whereas anhydrous organic solvents and water containing mobile phases have been found more useful for separating nonionic species. Mobile phase should be as simple as possible and prepared from the purest grade of solvent. The use of mixtures composed of more than four components of mobile phase should be avoided because of problems associated with reproducible preparations. In contrast to mobile phases of higher volatility, which are capable to evaporate quickly from the sorbent layer, better reproducibility is achieved with mobile phases of lower volatility. The mobile phases used as developers in TLC may be categorized into following groups.

Inorganic Solvents: Solutions of mineral acids, bases, salts and mixture of acids, bases and / or their salts.

Organic Solvents: Acids, bases, hydrocarbons, alcohols, amines, ketones, aldehydes, organophosphates and their mixture in different proportions.

Mixed Solvents: Above mentioned organic solvents mixed with water, mineral acids, inorganic bases or dimethyl sulphoxide and buffered salt solutions.

1.6 VISUALIZATION

Physical, chemical, enzymatic or biological detection methods are commonly used in TLC. A book by *Jork et al.* (17) is an excellent source of general information about physical and chemical methods of detection. Physical methods of detection involve the use of spectroscopy (autoradiography), X-ray fluorescence and UV radiation etc. Among physical methods, visualization under UV-light is most common. The chemical detection methods involve the spraying of plates with a suitable reagent, which forms colored compounds with the separated species. Alternatively, the reagent can also be taken in the mobile phase or in the adsorbent. In some cases, the detection is completed by inspecting the TLC plate after spraying with a suitable detection reagent under UV-light. Both selective and non-selective reagents may be used depending upon the requirement. However, reagents giving sufficiently sensitive color reactions with several species are generally preferred. The biological detection methods (bio-autography) are useful for specific detection of compounds with a certain physiological activity. An example is the detection of antibiotics on TLC plates using triphenyl-tetrazolium chloride and a microorganism that is sensitive to the antibiotic to be detected. Similarly, to detect antifungal compounds by TLC inhibition of fungal growth was assessed by the detection of dehydrogenase activity with thiazolyl blue. In addition to these techniques, enzyme inhibition, immunostaining and flame ionization detection methods have also been used.

1.7 QUALITATIVE ANALYSIS

(a) Identification: In TLC the identification of separated compounds is primarily based on their mobility in a suitable solvent, which is described by the R_F value of each compound. Where

$$R_F = \frac{\text{Distance of solute motion from the origin}}{\text{Distance of solvent motion from the origin}}$$

The factors which influence the magnitude of R_F are nature of sorbent and mobile phases, layer thickness, activation temperature, sample volume, chamber saturation, relative humidity and mode of development technique. Another term R_m which is the logarithmic function of the R_F value [i.e. $R_M = \log (1/R_F - 1)$] is more useful as it bears a linear relationship to some TLC parameters or structural element of the analyte. However, in case of continuous and multiple development, where the solvent front is not measured, the term Rx.

$$[R_x = \frac{\text{Distance moved by solute}}{\text{Distance moved by standard}}] \text{ is used}$$

R_F value ranges from 0.0 for a zone not leaving the point of application to 0.999 (≈1.0) for zone migration with solvent front. Unlike R_F, Rx value can be greater than 1.0.

(b) Separation: When two or more analytes have differential migration with the same chromatographic system. They are mixed thoroughly, the mixture is spotted on the TLC plate and chromatographed. The separated components of mixture are detected and their R_F values are recorded. Some of the basic requirements for a good separation arc (a) each spot should be compact ($R_L - R_T < 0.3$), (b) the difference in R_F values of two adjacent spots should be at least 0.1.

(c) No complexation should occur between/among separable species and

(d) Chromatography of individuals and the mixture should be

performed under identical experimental conditions.

1.8 QUANTITATIVE ANALYSIS

The three main approaches related to quantitation TLC include visual estimation and spot-size measurement, zone elution and in-situ densitometry.

Visual Estimation and Spot-Size Measurements: This is the simplest method of semiquantitative analysis. TLC plates with a definite sample aliquot along side standards containing known weights of analyte are simultaneously developed. After detection, the weight of analyte in the sample is estimated by visual comparison of the size and intensity of the standards and sample zones. The visual comparison works well if the applied amounts of sample are kept close to the detection limit and the sample is accurately bracketed with standards. The accuracy and reproducibility of this method falls in the range of 10-30%.

To standardize the quantification methods in TLC, *Mohammad* and *Fatima* (18, 19) *Mohammad* and *Tiwari* (20), *Nanda* and *Devi* (21) and *Mlodzikowski* (22) have established a linear relationship between the size of the spot and the amount of the analyte.

1.9 ADVANTAGES OF TLC

TLC is the most versatile and flexible chromatographic method. It is rapid because pre-coated layers are available for use as received, without preparation. It has highest sample throughout, because up to 30 individual samples and standards can be applied to a single plate and separated at the same time. The automated sample applications and developers allow high accuracy and precision in quantification. There is a wide choice of layers, developers and detection methods. The wide choice of detection reagents leads to unsurpassed specificity. Less pure samples can be successfully analyzed, as the layers are normally not reused. Being an "offline" method, different steps of the procedure are carried out independently.

1.10 COMBINATION OF TLC WITH OTHER ANALYTICAL TECHNIQUES

The careful combination of TLC with other analytical techniques is more useful to collect information regarding the analysis of a complex sample. Spectrophotometry, high-performance liquid chromatography (HPLC) and gas chromatography (GC) in conjugation with TLC are the three most widely used techniques. However, mass/GC, infrared and thermal analytical techniques in combination with TLC has also been used. One of the newest techniques used in combination with TLC is photoaccuoustic spectrometry, which is capable to locate compounds *in-situ* on the plate. *Issaq* and *Barr* (23) combined TLC with flameless atomic absorption spectrometry (FAAS) to identify an inorganic compound in an impure organometallic complex and to determine the recovery and purity of organometallic samples.

The examples cited above reveal, how the separation methods of TLC complement the analytical methods necessary for the absolute identification of a substance. TLC provides an excellent purification method for separating a substance of interest from other contaminants in the sample. Analytical techniques can then be applied to identify the separated substances.

1.11 SURFACTANT:

The term, surfactant, was originally registered as a trademark for selected surface active products [24] and later it was released to the public domain [25]. Soaps (salt of fatty acids containing at least eight carbon atoms) and detergents are surfactants whose solutions have cleansing properties. Surfactants are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8 – 18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can be nonionic, ionic or zwitterionic. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tend to squeeze the hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic.

Surfactants, when present at low concentration in a system, have the property of adsorbing onto the surface or interfaces of the system. The term interface indicates a boundary between any two immiscible phases: the term surface denotes an interface where one phase is a gas, usually air. The interfacial free energy is the minimum amount of work to create unit area of the interface or to expand it by unit area. The greater the dissimilarity in the nature of the two phases at the interfaces, the greater the interfacial (or surface) tension between them.

Most of the surfaces are negatively charged. Therefore, if the surface is to be made hydrophobic (water-repellant), then the best type of surfactant to use is a cationic surfactant, which will adsorb onto the surface with its positively charged hydrophilic head oriented towards the negatively charged surface (electrostatic attraction) and its hydrophobic group oriented away from the surface, making the surface water-repellant. The cationic surfactants should be avoided, if the surface is to be made hydrophilic (water-wettable). If the surface is positively charged, then anionics surfactants will, make it hydrophobic. The use of anionic surfactants should be avoided if the surface is to be made hydrophilic. Nonionic surfactants adsorb onto surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of the surface. If polar groups capable of H-

bonding with the hydrophilic group of the surfactants are present on the surface, the surfactant will probably be adsorbed with its hydrophilic group oriented towards the surface, making the surface more hydrophobic. If such groups are absent from the surface, then the surfactant will probably be oriented with its hydrophobic group toward the surface, making it more hydrophilic. Zwitterionic surfactants, carry both positive and charges without changing the charge of the surface significantly.

The hydrocarbon-based surfactants, on substituting with fluorocarbon into its structure create a molecule that is resistant to oxidation. Because of the smaller size of fluorine compared to the hydrogen atom, the fluorocarbon surfactants are more rigid in structure. They show strong surface tension lowering action, high water and oil repellency, better thermal and chemical resistance and good lubricating ability [26]. An application of hybrid fluoride-hydrogen containing surfactant is in water-based paints. Adding silicon into fluorine containing surfactants creates high quality lubricants, good defoamers and even molecules with a high anti-HIV(Human Immuno Deficiency Virus) activity [26]. There is also a group of surfactants known as microbial or biosurfactants, which have some very interesting and complicated structures. The production of biosurfactants is expensive compared to chemically synthesized surfactants [27, 28].

The most exciting developments in the field of surfactant chemistry are the emergence of the ***Gemini surfactants*** in the late 1980s and early 1990s. The term ***Gemini surfactants***, coined by Menger [29], has become accepted in the surfactant literature for describing dimeric surfactants, that is, surfactant molecules that have two hydrophilic groups and tails per molecule [29, 30]. These twin parts of the surfactants are linked by a spacer group of varying length (most commonly a methylene spacer or an oxyethylene spacer).

Gemini surfactants posses a number of superior properties when compared to conventional single-headed, single-tailed surfactants, the ***Gemini*** tending to exhibit lower critical micelle concentration (cmc) values, increased surface activity and lower surface tension at cmc, enhanced solution properties such as hard water tolerance, superior wetting times and lower kraft points. Because of these advantageous performances advantage of ***Gemini surfactants*** one can anticipate their usefulness in a myriad of surfactant applications (eg. soil remediation, oil recovery and commercial detergents), given a favourable cost/performance ratio.

1.12 CLASSIFICATION OF SURFACTANTS:

Depending upon the nature of the hydrophilic group, surfactants are classified as anionic, cationic, nonionic and zwitterionic surfactants.

Anionic Surfactants

These are the most widely used class of surfactants in industrial applications [31, 32]. Due to their relatively low manufacturing cost anionic surfactants are used in practically all types of detergents. The anionic surfactant is the reaction product of an organic compound (high molecular weight acid or alcohol) with an inorganic compound (sodium hydroxide or sulfuric acid), wherein the organic part of the molecule has a negative charge and the water-soluble (hydrophilic) part of the molecule has a positive charge. For example, soap (an anionic surfactants) has the following structure:

$$(C_{11}H_{23})CO^{-}Na^{+}$$

Similarly the reaction product of a long chain alcohol and sulfuric acid, neutralized with sodium hydroxide has the following structure:

$$(C_{11}H_{23})OSO_3^{-}Na^{+}$$

The anionic surfactants have the advantage of being high and stable foaming agents; however, they do have the disadvantage of being sensitive to minerals and the presence of minerals in water (water hardness) or pH changes.

Types of Anionic Surfactants

1. **Carboxylic acid salts:**
   - Sodium and potassium salts of straight chain fatty acids, $RCOO^{-}M^{+}$ (soap)
   - Amine salts
   - Acylated amino acids
   - Acylated polypeptides
   - Polyoxyethylenated (POE) fatty alcohol carboxylates (alkyl ether carboxylates), RO $(CH_2CH_2O)_xCH_2COOM$ (x = 4, usually)

2. **Sulfonic acid salts:**
   - Linear alkylbenzenesulfonates (LAS), $RC_6H_4SO_3^{-4}M^{+}$
   - Higher alkylbenzenesulfonates, C_{13}-C_{15}
   - Benzene -, toluene -, xylene - and cumenesulfonates
   - Lignin sulfonates

- Petroleum sulfonates
- N-acyl-n-alkyltaurates, $RCON(R')CH_2CH_2SO_3^{-4}M^+$
- Paraffin sulfonates, secondary n-alkane sulfonates (SAS)
- α-olefin sulfonates (AOS)
- Amylalkanesulfonates, $R(CH_2)_mCH(\Phi R')(CH_2)_nSO_3^-$
- Sulfosuccinate esters, $ROOCCH_2CH(SO_3^-M^+)COOR$
- Alkyldiphenyl ether (di) sulfonates (DPES), $RC_6H_3(SO_3^-Na^+)OC_6H_4SO_3^-Na^+$
- Alkyl naphthalene sulfonates
- Naphthalenesulfonic acid-formaldehyde condensates
- Isothionates, $RCOOCH_2CH_2SO_3^-M^+$

3. **Sulfuric acid ester salts:**
   - Sulfated primary alcohols (AS), $ROSO_3^-M^+$
   - Sulfated polyoxyethylated (POE) straight chain alcohols (AES), $R(OC_2H_4)_xSO_4^-M^+$
   - Sulfated triglyceride oils (sulf[on]ated oils)
   - Fatty acid monoethanolamide sulfates, $RCONHCH_2CH_2OSO_3^-Na^+$
   - Polyoxymethylenated (POE) fatty acid monoethanolamide sulfates, $RCONHCH_2CH_2O(CH_2CH_2O)_2SO_3^-Na^+$
4. **Phosphoric acid and polyphosphoric acid esters, $R(OC_2H_4)_xOP(O)(O^-M^+)_2$ and $[R(OC_2H_4)_xO]_2P(O)O^-M^+$**
5. **Flourinated anionics:**
   - Perfluorocarboxylic acids
   - Fluorinated polyoxetanes

Cationic surfactants

These surfactants are formed when alkyl halides react with primary, secondary or tertiary fatty amines. The water-insoluble (hydrophobic) part of cationic surfactants molecule has a positive charge and the water-soluble (hydrophilic) part is negatively charged as shown below:

$C_{16}H_{33}N^+(CH_3)_3Br^-$

Cetyltrimethylammonium bromide

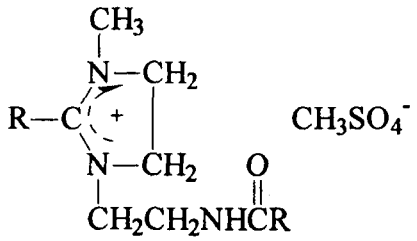
These surfactants reduce surface tension and are used as wetting agents in acid media. However, a disadvantage of cationic surfactants is that they have no

detergent action when formulated into an alkaline solution. They are incompatible with most anionic surfactants, but they are compatible with nonionic and zwitterionics.

Because of their tendency to adsorb at negatively charged surfaces, cationic surfactants have several important applications such as anticorrosive agents for steel, flotation collectors for mineral ores, dispersents for inorganic pigments, antistatic agents for plastics, hair conditioners, fabric softners, anticaking agent for fertilizers and as bactericides.

Types of cationic surfactants

1. **Long chain amines and their salts, $RN^+H_3X^-$**
2. **Acylated diamines and polyamines and their salts**
3. **Quarternary ammonium salts**
   - N-alkyltrimethylammonium chlorides, $RN^+(CH_3)_3Cl^-$
   - N-benzyl-n-alkyldimethylammonium halides, $RN^+(CH_2C_6H_5)(CH_3)_2Cl^-$
   - Dialkyl dimethylammonium salts, $R_2N^+(CH_3)_2Cl^-$
   - Imidazolium salts



   - Triethanolamine ester quats (TEAEQ), $R(O_2CH_2CH_2)_2N^+(CH_3)CH_2CH_2OH.CH_3SO_4^-$
4. **Polyoxyethylenated (POE) long chain amines, $RN[(CH_2CH_2O)_xH]_2$**
5. **Quarternized POE long chain amines, $RN(CH_3)[(C_2H_4O)_xH]_2^+Cl^-$**
6. **Amine oxides, $RN^+(CH_3)_2O^-$**

Nonionic surfactants

These surfactants have a hydrophobic/hydrophilic balance and hence there is neither a negative nor a positive charge on either part of the surfactant molecule. These surfactants have the advantages of being not affected by water hardness or pH changes. They are considered as medium to low foaming agents and are useful when a very low foaming surfactant is required. The chemical structure of a nonionic

surfactant in the (reaction product of lauryl alcohol and ethylene oxide) is shown below.

$$C_{12}H_{25}\text{-}(OCH_2CH_2)_x\text{-}OH$$

Nonionics are compatible with all other types of surfactants. Generally available as 100% active material free of electrolyte. POE nonionics are generally excellent dispersing agents for carbon.

Types of nonionic surfactants

1. **POE alkylphenols, alkylphenol "ethoxylates" (APE), $RC_6H_4(OC_2H_4)_xOH$**
2. **POE straight chain alcohols, alcohol "ethoxylates"(AE), $R(OC_2H_4)_xOH$**
3. **POE polyoxypropylene glycols**
4. **POE mercaptans, $RS(C_2H_4O)_xH$**
5. **Long chain carboxylic acid esters**
   - Glyceryl and polyglyceryl esters of natural fatty acids
   - Propylene glycol, sorbitol and POE sorbitol esters
   - Polyoxyethylene glycol esters and polyoxyethylenated (POE) fatty acids (including tall oil)
7. **Alkanolamine "condensate", alkanolamides**
   - 1 : 1 alkanolamine fatty acid "condensates"
   - 2 : 1 alkanolamine fatty acid "condensates"
8. **POE silicanes**
9. **N-alkylpyrolidones**
10. **Alkylpolyglycosides**

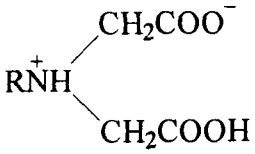
Zwitterionic surfactants

These surfactants contain both cationic and anionic groups [33]. They are compatible with all other types of surfactants less irritating to skin and eyes and adsorbed onto the negatively or positively charged surfaces without forming hydrophobic film. The main characteristic feature of zwitterionic surfactants is their dependence on the pH of the solution in which they are dissolved and hence on this basis they are subdivided into two groups as follows:

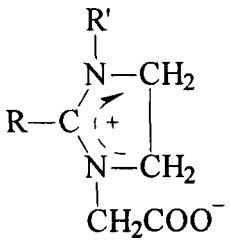
1. pH sensitive zwitterionics

These are ampholytic materials, which may show the properties of anionics at high pHs and those of cationics at low pHs. In the vicinity of their isoelectric point, they exist mainly as zwitterionic and show minimum solubility in water and minimum foaming, wetting and detergency.

- β-N-alkylaminopropionic acids, $RN^{+}H_2CH_2CH_2COO^{-}$
- N-alkyl- β-iminodipropionic acids,



- Imidazoline carboxylates,



- N-alkylbetaines, $RN^{+}(CH_3)_2CH_2COO^{-}$
- Amidoamines and amidobetaines
- Amine oxides, $RN^{+}(CH_3)_2O$

2. pH insensitive zwitterionics

These materials are zwitterionics at all pH values.

- Sulfobetaines, sultaines, $RN^{+}(CH_3)_{2(}CH_2)_xSO_3^{-}$

1.13 Analytical methods for surfactants:

The analysis of commercial surfactants is greatly complicated by the fact that these products are mixtures. Many and procedures used for the quality control and quality assurance of these products are based on classical methods of analysis; however, need for improved precision and accuracy have lead to increased use of instrumental analysis. Each surfactant has been analyzed with respect to the uniformity of the alkyl chain by various techniques such as TLC, HPLC and GC. Probably the most basic measurement for anionic and cationic surfactants involves the determination of active material using a two phase titration. These methods require chlorinated solvents and precision suffers because of end point ambiguity

from analyst to analyst. The photometric end point [34] and selective ion electrode to detect end point [35] have been used to avoid these problems. Probably the most common analyitical method for the analysis of anionic surfactants is Epton's two-phase titration method [36, 37], or one of its variations [38, 39]. Related single phase titrations can be performed and mentioned by either surface tension [40] or surfactant sensitive electrode [41-45] measurements. End points have been also detected by turbidity and refractive index changes [46]. Nonionic surfactants may be analyzed by titration after the addition of an activator, such as barium chloride, which forms complex, essentially a pseudo-cationic molecule, detectable by a surfactant-sensitive electrode [46]. Gronsveld and Faber [47] have recommended the adaptation of the titration method to oleic phase samples. In addition, infra red spectroscopy [48-50], nuclear magnetic resonance spectroscopy [51, 52], innovative ionization methods (fast atom bombardment, thermospray, electrospray, particle beams and matrix assisted laser desorption ionization-time of flight mass Spectroscopy [53] have also been used for the analysis of surfactants. The Table 1.2 lists some analytical methods that have been applied to the different surfactant classes [54].

1.14 Applications of surfactants:

Surfactants find widespread importance in the detergent industries, emulsification, lubrication, catalysis, tertiary oil recovery and in drug delivery. In analytical chemistry, surfactants have been recognized as being very useful for improving analytical methodology e.g. in chromatography and luminescence spectroscopy [55, 56]. Aqueous surfactant micellar systems have been utilized successfully in virtually every area of analytical chemistry. Separation applications, for example, have utilized micellar phases as mobile phase additive in thin layer chromatography, HPLC and capillary electrophoresis (CE). In addition, several myriad of techniques have been developed that utilize the solubilization capacity of micelles in purification, pre-concentration and extraction processes [57]. Some of the important uses of surfactants in analytical chemistry are summarized,

Table 1.2 : Typical methods used in surfactant analysis

Surfactant Class	Method
Anionic	
Alkyl sulfates and sulfonates	Two-phase or surfactant-electrode monitored titration
Petroleum and lignin sulfonates	Column or gel permeation chromatography
Phosphates esters	Potentiometric titration
Sulfosuccinate esters	Gravimetric or titration methods
Carbohydrates	Potentiometric titration or two-phase titration
Nonionic	
Alcohols	NMR or IR spectroscopy
Ethoxylated acids	Gas chromatography
Alkanolamides	Gas chromatography
Ethoxylated amines	Potentiometric titration
Cationic	
Quarternary ammonium salts	Two-phase or surfactant-electrode monitored titration or GC or HPLC
Zwitterionic	
Carboxybetaines	Low pH two-phase titration, gravimetric analysis or potentiometric titration
Sulfobetaines	HPLC

1. Micellar mobile phases were used for the separation of a mixture of polycyclic hydrocarbon [58, 59]; pesticides [60, 61]; nucleotides [60]; anthraquinone and 1,4-naphthaquinone; vitamins K_1 and K_5 [61]; o-,m-,p-aminophenols [62]; aminoacids [58, 63]; p-nitrophenol and p-nitroaniline [64, 65]; phenol, resorcinol, pyrogallol, pyrocatechol and hydroquinone [59, 62]; bromocresol green, methyl orange, methylene blue and fluorosceine [62]; substituted benzoic

acids [64]; food dyes and indicators [59, 66]; 1- and 2-naphthol; naphthalene-2-carboxylic and naphthalene-2-sulphonic acids [59]; 33 medicianl substances, sulfanilamides, antipyrites, vitamin B and adrenaline [67]; ten fluoroscein derivatives [68, 69]; zinc (II); cadmium (II) and mercury (II) [70]; silver; copper; and gold [71]; copper (II); nickel (II); cobalt (II, III) and iron (III); 1,3-diketones [72] and ions of these metals [73]. Other applications of surfactants include their use in estimating the purity of xylenol orange [74]; chromazural S and phenol carboxylic acids of the triphenyl methane series [75, 76] and other organic reagents and acid-base indicators [77].

2. In electrophoresis, various techniques require the use of surfactants. The popular technique of SDS-PAGE (Poylacrylamide gel electrophoresis) for the identification and subunit molecular weight estimation of proteins is based on a specific type of surfactant-protein interaction [78]. 2D-PAGE uses SDS in one direction and triton-X 100 in the other. This technique has been used to identify proteins containing long hydrophobic regions [79] and relies on the differential binding ability of nonionic surfactants to water-soluble and intrinsic membrane proteins. Isoelectric focusing [80], native electrophoresis and blotting [81] are other electrophoretic techniques which may need surfactants for the solubilization or transfer of membrane proteins.
3. In high performance liquid chromatography, common techniques such as, ion exchange HPLC, reversed-phase HPLC and size exclusion-HPLC may require surfactants to solubilize membrane proteins [82, 83]. Ion pair HPLC requires surfactants as reagents in order to achieve the separation conditions [84, 85].
4. Affinity surfactants have been used as reversibly bound ligands in high performance affinity chromatography [86].
5. The contamination of the ground water by non aqueous phase liquids (NAPLs), such as tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane is a problem of high concern. These substances are difficult to remove, and have low biodegradability [87]. These organic toxic liquids can persist in the soil for many decades and offer a long term threat to ground water quality [88]. The use of surfactants to remediate ground water contaminated non aqueous phase liquids has been under significant development and field testing over the last two decade especially for dense non aqueous phase ligands such as chlorinated solvents [89, 90]. The techniques used to achieve the displacement, solubilization and flushing

of the NAPLs are adapted from surfactants based enhanced oil recovery technology [91, 92].

6. In the petroleum industry, applications of surfactants include [93, 94], wettabilty alteration, enhanced micro displacement of oil, stabilizing foams for mobility control or foam drilling fluids, stabilizing emulsions or foams for acids stimulation, separation and floatation aids in oil sand processing, heavy oil transportation as aqueous emulsion, surfactant enhanced aquifier remediation and breaking of oil spill emulsions.
7. Surfactants played an important role in biological systems. The pulmonary surfactant systems, although discovered in 1929, have only been applied clinically around 1990 for the treatment of respiratory distress syndrome. Surfactants replacement therapy may also be used in treating other forms of lung disease, such as meconium aspiration syndrome, neonatal pneumonia and congenital diaphragmatic hernia [95]. For lung surfactants composed of phospholipids and proteins [96, 97], it is necessary to maintain a low surface tension at the alveolar air-liquid interface. The lung surfactants system may also protect lung from injury and injury and infection caused by inhalation of particles and micro-organisms [95, 97].
8. Quaternary ammonium surfactants (cationic surfactants) have potent germicidal activity in addition to their use as fabric softners in detergents. The best known fabric softners and antistatic agent is ditallow dimethyl ammonium chloride (DTDMAC). Emulsifiers commonly have an N-alkyltrimethyl ammonium chloride or N-alkylimidazoline chloride configuration whereas, germicides, (e.g. benzalkonium chloride, have an N-alkydimethyl benzyl ammonium chloride structure.
9. Surfactants are involved in the production of many common food items and can be found in the extraction of cholesterol, solubilization of oils, liquor emulsification, prevention of component separation and solubilization of essential nutrients.
10. The formation of pesticides is significant in terms of product stability and product performance. Some of the typical surfactants used in pesticide formulations are ethoxylated alcohols, alkyl phenols, sorbilan acid alkylamines [98]. Organosilicone surfactants have begun appearing in commercial spray application products [98]. The latter show improved surface tension lowering

(for improved leaf wetting) and a low dynamic surface tension (for spray drop retention or leaves) [98]. The organosilicone surfactants easily break down, which is an environment bonus but the lack of stability poses difficulty in product storage as ready to use products [98].

1.15 Literature

Literature appeared during 1989 – 2005 on analysis of surfactants by various analytical techniques as presented in Table 1.2.

Table 1.2: Literature appeared during 1989 – 2005 on analysis of surfactants by various analytical techniques.

Title	Analyte	Technique	Remarks / Comments	References
Classification and analysis of surfactants products by simple laboratory techniques	Ionic and nonionic surfactant	Colorimetric method and TLC method	Ionic and nonionic surfactants are identified by calorimetric methods using reagents Ce-nitrate, $CHCl_3/AlCl_3$, aq. Br, $KMnO_4$, alc. KOH and acetic anhydridal H_2SO_4. Solvent extraction was used to isolate surfactants from formulations. TLC methods were used to separate ionic and nonionic surfactants in detergents	1
Separation , identification and determination of alkyl and alkylphenol ether carboxylates by HPLC	Anionic, nonionic or amphoteric	UV-spectrophotometer, differential refractometer and HPLC	The separation is carried out by HPLC using a reversed phase RP-18 column and a mixture of MeOH, water and MeCN with addition of ion pairing reagent as mobile phase. For detection and quantitative determination a differential refractometer is used and alkyl phenol ether carboxylates are to be determined by UV-spectrphotometer	2

1. V. Perez; A.G. Arce; L. Maria, Tec Lab, 1989, 12, 236-245.

2. H.Koenig; W.Strobel, J.Anal.Chem, 1990, 338, 728-731.

Title	Analyte	Technique	Remarks / Comments	References
Spectrophotometric determination of hydrophobic anionic surfactant with basic dyes in aqueous solutions	Anionic surfactants such as NaC_{10}-C_{16}-alkyl sulfates, alkylarylsulfonates, naphthalene sulfonates and alkyl succinamino sulfonates	Spectrophotometer	Determination of anionic surfactant in aqueous solutions, using basic dyes of the triphenylmethane , azine and thiazine. The limit of determination of the surfactant increased with increasing length of the alkyl group, as well as with increasing molecular weight of the dye containing upto molecular weight 370, approximately due to increasing stability of the ionic assoc. formed in the system studied. Determine anionic surfactants in the presence of methylene violet and crystal violet	3
Effect of nature of support and impregnating agent on a Lipophilicity determination for nonionic surfactants by reverse phase thin layer chromatography	Nonionic surfactant	TLC	The retention of 9 nonyl phenyl ethoxylate oligomers was determined in 15 reverse phase chromatographic system using silicone oil of various molecular weight as impregnating agents and silica, cellulose and alumina supports. The retention values did not follow the additivity rule and they did not change linearly with increasing length of the ethylene oxide chain. Probably due to the folded state of the chain in the eluent. Retention increasing with increasing level of impregnation	4

3. A.T.Pilipenko; S.A.Kulichenko; S.A.Dolenko, Khim Technol Vody, 1990, 12, 623-627.

4. T.Cserhati;Z.Illes, Chromatographia, 1991, 31, 152-156.

Title	Analyte	Technique	Remarks / Comments	References
The identification of anionic detergents by thin layer chromatography	Anionic surfactant	TLC method	Surfactants were identified by TLC on silica gel plates using BuOH-HOAC-iso PrOH (3:1:0.5) solvent system and azure and Dragendroff reagent for visualization under UV light. Detection limit 2 μg	5
Separation of fatty components by solid phase adsorption part II. Determination of fatty substances on fat liquoring baths other applications	Fatty components	TLC method	Used silica gel, alumina or other solid support which is impregnated for determination of fatty substances, promitas reactions such as hydrolysis and esterification. The method was used for analysis of flat liquoring baths from natural and synthetic fats to determine residual fat in hides and wet blue leather. Method eliminates emulsification between the liquid and the polar phases, requires low solvent vol and is reproducible	6

5. S.Akinci; K.C. Guven, Acta Pharma Turc, 1992, 34, 121-126.

6. J.Cat; M. Fort; J.Cartiel, AQEIC Bol. Tec., 1992, 43, 147-157, 162-167.

Title	Analyte	Technique	Remarks / Comments	References
Pressure tuning Fourier transform infrared and Raman spectroscopy of anionic surfactants	Anionic surfactant	FTIR and Raman spectroscopy	Describes novel pressure tuning FTIR and Raman spectroscopic techniques to study aqueous surfactant solution and discuss Na and k decanoate and Na Oleate in detail with micellar solutions of anionic surfactants	7
Hydrogen-1 NMR self study for mixed micelles of fluoro carbon and hydrocarbon surfactants	Fluorocarbon abd hydrocarbon surfactans	NMR technique	Technique used to study the variation of monomer concentration and micellar size in fluorocarbon hydrocarbon surfactant mixed systems such as Liperfluorooctanedulsunfate (LiFOS)-Li dodecyl sulfate and Na perfluorooctanoate. The self diffusion coefficients of micelles depend on the micelles composition and LiCl concentration. An addition of LiCl induced a micellar growth. In higher liCl concentrations, the micellar size of LiDS was increased with mixing of LiFOS	8

7. T.T.P.Wang; H.H.Mantsch, ACS Symp. Ser., 1990, 447, 44-55.

8. T. Asakawa; T.Imae; S.Ikeda; S.Miyagishi; M.Nishida, Langmuir, 1991, 7(2), 262-266.

Title	Analyte	Technique	Remarks / Comments	References
Liquid chromatographic determination of linear alkyl benzene sulfonates in aqueous environmental samples	Anionic surfactant (LABS)	HPLC	Determine LAS in influent or effluent waste waters, river waters. LAS are desorbed by a specific organic solvent mixture. The extract is dried and the residue constituted with 0.5ml of a water/MeoH mixture, super cosil CsDB material was chosen as stationary phase because it combined all of the isomers of each LAS homologue into a single peak. This simplifying interpretation of the chromatograms and enhancing the detection levels	9
Separation and determination of ethoxylated nonionic surfactants by HPLC	Nonionic surfactant	HPLC	Simple technique make possible to calculate the molecular weight distribution of ENPs using only 2 parameters i.e. retention time or peak height. Molecular weight distribution curves were determined for a series of compound ENPs with a degree of ethoxylation 4, 6 and 10	10
Determination of anionic surfactant in aqueous environmental samples by flow injection analysis with chemiluminiscence detection	Nonionic surfactant	Flow injection analysis with chemiluminiscence detection	Flow injection for determination of a compound available fatty amine ethoxylate base nonionic surfactant	11

9. A.Dicocia; M.Marchetti; P.Sampari; M.Antonio, Anal. Chem., 1991, 63, 1179-1182.

10. I.L.Kazakeuich; A.V.larin, Zh. Anal. Khim., 1991, 46, 374-379.

Title	Analyte	Technique	Remarks / Comments	References
Reversed-phase High performance liquid chromatographic method for the assay of 1,4-dioxane in sulfated polyoxyethylene alcohol surfactant	Polyoxyethylene alconol	HPLC method and UV detection	Using baker bond Gs catridges, samples were directly analysed on a lichrosphere CH-8 reverse phase column with UV detection at 200 nm MeOH-water eluent. Procedure is simple, reproducible, specific and suitable for routine analysis of common surfactants	12
Application of carbon-13 NMR in surfactant analysis	Surfactants	Carbon-13 NMR	Application in determination of structure, quant, analysis of compn. and physical properties of surfactants	13
Cationic surfactants in waste water and activated sludge	Cationic surfactant	HPLC method	HPLC with a cond. Detector is presented	14

11. S.J. Lancaster; J.P.Worsfold, Anal. Chem. Acta, 1990, 239, 189-194.

12. S.Scalia, J. Pharm. Biomed. Anal., 1990, 8(8-12, 867-870.

13. M.Jiewi, Riyong Huaxue Gongye, 1990, (1), 24-8.

14. M.Emmrich, K.Levsen, Vom Wasser, 1990, 75, 343-349.

Title	Analyte	Technique	Remarks / Comments	References
Characterization of cationic surfactant markers and their abiotic degradation products by CGC-EI/PICI MS	Cationic surfactant	CGC-EI/PICI MS	The electronic impact (EI), pos ion chem. Ionization (PICI) mechanisms of secondary and tertiary trialkyl amines were detected	15
Determination of surface active anionic and nonionic material content in sandy soils by a spectrophotometric method	Anionic and nonionic surfactant	Spectrophotometric method	SDS and Na lauryl sulfate and nonionic surfactant such as poly ethylene glycol p-nonyl phenyl ether and poly ethylene glycol lauryl ether were detected in sandy soil and relative standard deviation is obtained	16
Application of infra red and Raman spectroscopy to the study of surface chemistry	Surfactant	Raman and IR spectroscopy	It include surfactants and their aqueous solution film and adsorbed molecules at gas solid and liquid solid interfaces	17

15. M.Valls; J.M.Bayma, Fresenius J. Anal. Chem., 1991, 339(4), 212-217.

16. L.Sujbert, Agrokem Talaytan, 1990, 39(1-2), 183-190.

17. T. Takenaka; J.Umemura, Vib. Spectra Struct., 1991, 19, 215-314.

Title	Analyte	Technique	Remarks / Comments	References
Studies on the color reaction of triphenyl methane basic dyes with anionic surfactants in aqueous solutions	Anionic surfactant	Spectrophotometric method	This method for the determination of surfactant is based on the formation of ions associations of basic triphenymethane dyes, such as malachite green, brilliant green in the presence of solubilizers. The conditions for the color reaction, sensitivity and selectivity were investigated	18
Improved and rapid method for the spectrophotometric determination of trace amounts of polyacrlamides in water	Nonionic, cationic and anionic	Spectrofluorometric	The polyacrlyamides are reacted with hypochlorite from either NaClO or chloramines T to produce amines, then it reacted with fluoroscamine to give fluroscent compounds. The procedure is proposed for the determination of the polyacrylamides in fresh and saline water. The overall time of determination is 24 h, previously reported as 48 h	19

18. S.Liu; Z.Huang;F.Ji, J. Surf. Sci. technol., 1990, 6(3), 223-229.

19. Y.arryanto; L.S.Bark, Analyst, 1991, 116, 1149-1153.

Title	Analyte	Technique	Remarks / Comments	References
Use of high performance liquid chromatography for analysis of mixtures of amphoteric surfactants	Amphoteric surfactants	HPLC	Amphoteric surfactant produced from fatty amines containing carboxyl group and alkyl group compound were detected in mixtures by HPLC using silica ODS column, with eluent aq MeOH/NaClO, at 50^0C, retention time was also determined. The method could be used for characterization of cosmetic formulations quickly and accurately	20
Analysis of anionic surfactants by HPLC with conductive detector	Anionic surfactant	HPLC	Analysis alkylbenzene sulfonates, α-olefin sulfonates and polyoxyethylene alkylether sulfate was performed by reversed phase chromatography using silica gel as stationary phase and 1 mM $NaClO_4$ in AcCN/water as mobile phase. Obtained calibration curve was linear in the range of 0.005-17 μg surfactant in common household and cosmetic products were analyzed with high sensitivity and selectivity	21

20. O. Cozzoli; D.Marini; F.Balestrieri, Riv.Ital. Sostanza Grasse, 1989, 66(5), 276-277.

21. Y. Kondoh, Yukagaku, 1991, 40(8), 671-677.

Title	Analyte	Technique	Remarks / Comments	References
Bile salts suefactants in micellar electrokinetic capillary chromatography (MECC) application to hydrophobic molecule separations	Bile salt surfactants	Application of MECC	Separation of various hydrophobic, separations of previously inter-reactable compounds including polyaromatic hydrocarbons. Effect of methanol on CMC investigated for SDS and bile salt sodium cholate. Structure of bile salt micelle is much more tolerant to the addition of organic solvents than SDS	22
In situ near infra red internal reflection spectroscopy for surfactant adsorption reactions using reactive internal reflection elements	Surfactant	Near IR internal reflection spectroscopy	NIR can be used to quantify surfactant adsorption reaction in situ. The adsorption of Na oleate was studied on fluorite and on calcite	23

22. R.O.Cole; M.J.Seapniak; W.L. Hinze; J. Gorse; K.Oliges, Energy Res. Abstr., 1991, 16(3), Abstr no. 7865.

23. J.J.Kellar; M.W.Cross; J.D. Miller, Appl. Spectrosco., 1990, 44, 1508-1512.

Title	Analyte	Technique	Remarks / Comments	References
Thin layer chromatographic method for quantitative and qualitative studies on surfactant containing preparations	Surfactants	TLC method	Determination of cations, anions and other surfactants in cosmetics is described	24
Lutetium-methyl thymol blue-cetyl pyridium complex for determining different type of surfactant	Cationic and nonionic surfactant	Spectrometric	Determination of cationic surfactants by Bathochromic shift. The break down of the ternary complex by anionic surfactant shifted the adsorption maxima to 610 nm, this finding was utilized for developing a method for determination of anionic surfactant. To alleviate the soly problem of hydrophobic association of cationic and anionic surfactant, the method required the presence of non ionic surfactants acting as solubilizing agents	25

24. G.Hohm, Anal. Kosmet, 1990, 155-180.

25. A.T.Pilipenko; S.A.Kulichenko; E.G.Maksimyak, Khim. Khim. Tekhnol, 1990, 33(11), 61-65.

Title	Analyte	Technique	Remarks / Comments	References
Use of an evaporating light scattering detector in reversed phase high performance lquid chromatography of oligomeric surfactants	Oligomeric surfactants	HPLC and light scattering detector	Sensitivity of the evaporative light scattering detector depended on the Analyte conc. and the organic modifier concentration under reversed phase gradient condition. Detection limit for alc. and carboxylic acid homologues were detected.	26
Highly efficient reversed phase HPLC studies of amphoteric and cationic amido group containing surfactants	Amphoteric and cationic amido group surfactants	HPLC	Retention properties and conditions of separation of homologous series of amido group containing amphoteric and cationic surfactants were studied by reversed phase HPLC. Retention capacity and length of alkyl chain of surfactant was detected by using equation log k' = Anc + B	27
HPLC analysis for surfactants as pesticide formulation	Anionic and nonionic surfactants	HPLC and ion exchange resin	Simultaneous and isocratic separation of the 4 surfactant type was achieved when ethoxylated tallow amines from the 2 other nonionic surfactant was achieved. Only after the separation of anionic components by means of ion exchanger resin surfactant examined in pesticides	28

26. Y.Mengerink; J.C.H.DeMan; S.Vanderwal, J. Chromatogr. 1991, 552(1-2), 593-604.

27. V.Allikmaa, Keem 1991, 40(1), 67-72.

28. T.Ban; E.Papp; J. Inczedy, Magy. Kem. Foly, 1991, 97(6), 246-249.

Title	Analyte	Technique	Remarks / Comments	References
Selective determination of cationic surfactants using the complex molybdenum (VI) pyrogallol red in water micellar solutions	Cationic surfactant	Spectrophotometric method	Selective determination of cationic surfactants using the complex molybdenum (VI) pyrogallol red in water micellar solutions.	29
NMR studies on aqueous solutions of surfactants	Surfactants	NMR	A review with 24 references of recent NMR studies on aqueous solutions of surfactants	30
Quantitative aspects of indirect UV detection in capillary zone elctrophoresis	Anionic surfactant sodiumalkyl sulfate (SAS)	UV detection and capillary zone electrophoresis	Excellent reproducibility of electrophoretic mobilities and linearity of detection signal can be obtained. System for analysis of common mixtures of primary (SAS) is demonstrated	31
Separation of dodecyl poly (oxyethylene) ethers and 2 (hydroxyl ethyl) dodecane amides by alumina column chromatography	Surfactants such as dodecyl poly (oxyethylene) ethers and 2 (hydroxyl ethyl) dodecane amides	HPLC	HPLC data for the mobile phase systems of EtOAc with water and with MeOH indicated linear relations. Change in retention time was noted. Elution behaviour should be applicable to the development of suitable methods for objective analysis	32

29. T.A.Pilipenko; N.G.Kulchenko, Ukr. Khim.Zh. 1991, 57(3), 236-241.

30. T.Kota, Yukagaku, 1992, 41(2), 75-81.

31. F.W.M.Nielen, J.Chromatgr., 1991, 588(1-2), 321-326.

32. H.Yoshimura; T.Sugiyama, Yakagaku, 1991, 40(12), 1120-1124.

Title	Analyte	Technique	Remarks / Comments	References
Spectrphotometric determination of cationic and anionic surfactants with anionic dyes in the presence of nonionic surfactants Part II: development of batch and flow injection method	Cationic and anionic surfactants	Spectrophotometric and flow injection method	Spectrphotometric determination of cationic and anionic surfactants with anionic dyes in the presence of nonionic surfactants Part II: development of batch and flow injection method	33
Electrochemical detection of surfactants for HPLC	Surfactants polyoxyethylene nonyl phenyl ether and POE mono lauryl ether	HPLC and UV detection	A comparison of characterstics of Au-Hg and Pt-Hg electrode as working electrode was investigated for the purpose of electrochem detection of surfactants in HPLC	34
Surfactants solubilization behavior head space analysis	Surfactants	Head space analysis and (AHGC)	Automatic Headspace Gas Chromatography is used to detect solubilization site within micelle for a solute, effect of solute partition coefficient and effect of cosolvent in CMC	35

33. S.Motomizu; M.Oshima; Y.Hosoi, Mikrochim Acta, 1992, 106(1-2), 67-74.

34. T. Matsuda; K.Niki;H.S.Y.Yokoyuma, Denki Kaguku Oyobi Kogyo Butsuri Kagoku, 1992, 60(1), 58-60.

35. N.J.Labows, J.Am.Oil Chem.Soc., 1992, 69(1), 34-38.

Title	Analyte	Technique	Remarks / Comments	References
New colorimetric assay procedure for polyoxyethylene nonionic surfactant	Nonionic surfactant	Colorimetric method	Factors such as validity of Beers law, stability of reagent and nature of the complex were studied for ethoxylated alkyl phenols	36
Optimization of a chromatographic post column ion pair extraction system for the determination of cationic tensides	Ionic surfactants	HPLC and post column ion pair extraction	A post column ion pair extraction system was optimized for the detection of ionic or ionizable organic compounds, especially cationic surfactants, in HPLC using this system. Those which have high selectivity and sensitivity can be detected	37
Determination of Triton-X 100 by HPLC	Nonionic surfactants	HPLC	Biodegraded and biodecomposition of surfactant can be evaluated by HPLC in a manner similar to the evaluation method based on the decrease of total organic carbon C.K.Nara	38

36. M.Aminuddin, H.D.C.Rapson, J. Chem. Soc. Pak., 1991, 13(1), 192-196.

37. M.Schoester; G.Kloster, Vom Wasser, 1991, 77, 13-20.

38. S. Murai; T.Mizunuma; T.Imajyo, Kenkya Hokoku-Kanagawaken Kogyo shinkensho, 1991, 62, 82-83.

Title	Analyte	Technique	Remarks / Comments	References
Reversed phase high performance liquid chromatography of anionic and ethoxylated nonionic surfactants and pesticides in liquid pesticide formulations	Anionic and nonionic surfactant	HPLC and anion exchange resin	Simultaneous and isocrate separation of ionic and nonionic surfactant (nonyl phenol fatty acid and fatty amine ethoxylates) can be achieved by RP-HPLC with an octyl silica gel as stationary phase and MeOH aqueous phosphate buffer eluents	39
Tarce analysis for cationic surfactants in water using HPLC with conductometric detection	Cationic surfactant	HPLC and conductometry	Simple and fast determination of trace amounts of compounds used cationic surfactants is described. After extraction from water the cationic surfactants are separated by HPLC and detected by conductometry	40
Determination of linear alkylbenzene sulfonate (LAS) in the river water containing domestic waste waters	Anionic surfactant (LAS)	HPLC and spectrophotometric method	Determination of LAS in river water using methylene blue by HPLC and spectrophotometric method. It was shown that the negative error of the photometry due to the presence of protein can be eliminated by adding n-proH as a suppressor for protein binding of LAS	41

39. T. Ban; E.Papp; J. Inczedy, J. Chromatogr, 1992, 593(1-2), 227-231.

40. L.Nitschke; R.Muellar;C.Metzner; L.Huber, Fresenius, J. Anal. Chem., 1992, 243(9), 711-713.

41. I.Fujita; T.Oda; T.Sugimura, Kumamoto-Ken Eisei Kogai Kenkyushoho, 1991, 20, 40-42.

Title	Analyte	Technique	Remarks / Comments	References
The composition of a variety of nonyl phenol poly (ethylene oxide) phosphate anionic surfactant	Anionic surfactant	FTIR, NMR and HPLC	The characterization of surfactant was carried out by FTIR, NMR and HPLC	42
Quantitative analysis of alkyl benzene sulfonate surfactants using continuous flow fast atom bombardment spectrometry	Anionic surfactant	Continuous flow fast atom bombardment and taden mass spectrometry and scanning	A quantitative method for the analysis of (LAS) has been developed using continuous flow fast atom bombardment and tanden mass spectrometry. LAS adsorbed to sludge was eventually degraded in the plants aerobic sludge digester (branched ABS can be determined by scanning	43
Extraction of nonionic surfactants from waste water using centrifugal partition chromatography	Nonionic surfactants	Centrifugal partition chromatography (CPC)	Extraction of nonionic surfactants from waste water into EtOAc using CPC	44
Interaction of hydrophobic anions with cationic dyes and its application to the spectrophotometric determination of anionic surfactant	Ionic surfactant	Spectrophotometry	Interaction of hydrophobic anions with cationic dyes and its application to thespectrophotometric determination of anionic surfactant	45

42. D.J.Frazier; D.R.Johnson; C. G.Wade; J.D.Oleary, Comun, jorn. Com.Esp. Detorg., 1991, 22, 99-110.

43. J.A.Borgerding; R.A.Hites, Anal. Chem. 1992, 64(13), 1449-1454.

44. A.R.Menges; S.T.Menges; L.G.bertrand, J. Liq. Chromatogr. 1992, 15(15-16), 2909-2925.

45. M.Oshima; S.Motomizu; H.Doi, Analyst, 1992, 117910), 1643-1646.

Title	Analyte	Technique	Remarks / Comments	References
Amphoteric determination of surfactants using a gold electrode modified with a self assembled monolayer of stearyl thiol	Surfactant	Use gold electrode	The concentration of surfactants containing C_{12} alkyl chains could be detected by changes in the current ratio using stearyl thiol coated Au electrodes in the presence of Fe^{3+} or ferricyanide marker ions	46
Determination of the molecular heterogeneity of nonionic surfactanta based on ethylene oxide by HPLC	Nonionic surfactant	HPLC	An express method for the determination of molecular weight distribution of ethoxylated alkyl phenol, synthetic fatty acids alcohols using reversed phase HPLC. Isononyl and octyl phenols, dodecyl alcohol and lauric acid are analyzed	47
Flow-injection method for the determination of anionic surfactants after liquid-liquid extraction using ontube visible absorption and fluorescence detection	Anionic surfactant	Liq-liq extraction, fluorescence detection, spectrphotometric (SM) and spectrofluorometric (SFM)	Anionic surfactants in water samples were determined by (SM) and (SFM) involving flow injection coupled with liq-liq extraction. Two kinds of dyes examined cationic and neutral dyes	48

46. T.Kawaguchi; H.M.Y.Yamauchi; H.Ohmori, Anal. Sci, 1992, 8(5), 651-652.

47. R.R.Dyakonova; E.P.chirko; I.M.Skipina; A.V.Ezrets, Zavod. Lab. 1991, 57(3), 5-7.

48. S. Motomizu; M.Kobayashi, Anal. Chim. Acta 192, 261(1-2), 471-475.

Title	Analyte	Technique	Remarks / Comments	References
Determination of surfactants by fluorimetry using several fluorescent dyes	Anionic surfactant (SDS) and cationic (zephiramine nonionic Brij-(58)	Fluorimetry, flow injection and spectrophotometry	For determination of SDS the method is based on an ion pair extraction reaction with methylene blue in O-$Cl_2C_6H_4$. SDS react with acridine orange 10-dodecyl bromide to quench its fluorescence. Zephiramine determined in the concentration range of 1 X 10^{-6} – 4 X 10^{-5} and Brij 58 (2 X 10^{-6} – 1 X 10^{-4})	49
Study of adsorbed surfactant layer at the solid/liquid interface using electron spin resonance spectroscopy	Surfactant	(ESR) electron spin resonance	ESR versatile tech for characterizing in situ surfactant layers adsorbed on oxide minerals (alumina) in both aqueous and non aqueous media	50
HPLC analysis of quaternary ammonium surfactants with the evaporative light scattering detection	Quaternary ammonium surfactant	HPLC	Separation of quaternary ammonium surfactants achieved on a bonded poly phenol silical gel column with gradient elution and evaporative light scattering. It is quantitative determination of low level of surfactant	51

49. T.Masadome; H.Ohura; N.ishibarhi, Ariake Kogyo Koto Senmon Gakko Kiyo, 1992, 28, 117-123.

50. C.A.Malbrel; P.Somasundaran, Inst. Conf. Fundam. Asrpt, 1989, 529-541.

51. J.A.Wilkes;G.Walravon; M.J.Talbot, J.Am. Oil Chem. Soc, 1992, 69(7), 609-613.

Title	Analyte	Technique	Remarks / Comments	References
Determination of modifiers in viscose and spinning bath	Cationic and nonoionic	Gravimetric (GM) and spectrophotometric method (SM)	Determination of surfactant by GM and SM additives in viscose were compared. GM based on precipitation of the additive by phosphinotungstic acid (SM) based on measuring the color intensity of the complex formed by reaction of cationic surfactantwith anionic dye	52
Tritrimetric method for the determination of cationic surfactants in industrial samples	Cationic surfactant	Titration method	The Analyte is determined by titration in the presence of an acid-base indicator. The indicator used is a mixture of xylenol blue and syntanol DS-10 with wt ratio of 1:130-180. titratia is performed at pH 9.6-9.8. an aqueous solution of surfactant is used as titrant	53
Indirect polarographic determination of trace amounts of nonionic surfactants	Nonionic surfactant	Polarographic method	Selected nonionic were transformed into complexes with molybdophosphoric. Method was used to determine nonionic surfactants in surface water and waste water	54

52. J.Jozwicka, Wlokna Chem., 1990, 16(2), 173-181.

53. V.V.Sukhan; S.A.Kulichenko; S.A.Dolenko; S.V.sidoruk, Izobreteniya, 1992, (6), 178.

54. I.Zjawiong; Z.Klima, Chem. Anal., 1991, 36(4), 741-747.

Title	Analyte	Technique	Remarks / Comments	References
Extracts for photometric determination of nonionic surfactants	Nonionic surfactant	Photometric determination	In photometric determination of nonionic surfactants extracted from samples by organic solvents	55
Qualitative analysis of anionic or cationic surfactants using surfactant electrode	Ionic surfactants	Potentiometric titration	Potentiometric titration allows to perform quantitative analysis of surfactants previously unattainable by ion pair extraction. The electrode used in the present study was a liquid membrane ion exchange Ag/AgCl electrode	56
Potentiometric determination of ionic surfactant in cosmetics and household products	Ionic surfactants	Potentiometric titration	The ionic surfactant content of cosmetics and household products was determined by potentiometric titration using two different liquid membrane surfactant electrode and a coated wire electrode	57
Spectrophotometric determination of cationic and anionic surfactants with anionic dyes in the presence of nonionic surfactants Part I; a general aspect	Ionic surfactant	Spectrophotometric method	The behaviour of color development of anionic azo dyes, methyl orange and its analogues was examined in aqueous media by changing the microenvironment of the dyes. Methods for the determination of organic onium ions and anionic surfactants were proposed	58

55. V.L.Parkhomovskii; A.E.Gorshitein; I.V.Timofeeva; M.Yu. bakinova; M.Z.Vinsthtein, Otkyrtiya Izobret, 1991, (33), 159.

56. Y.hans H. Oei; I.Mai; D.C.Toro, 1991, 42(5), 309-316.

57. D.Lowy; A.Patrut; A.FlorinDan; F.Ovari; M.Watter, Magy Kem. Foly, 1991, 97(11), 460-465.

58. S.Motomizu; M.Oshima; Y.Hosoi, Mikrochim Acta, 1992, 106(1-2), 57-66.

Title	Analyte	Technique	Remarks / Comments	References
The use of HPLC in determination of aromatic sulfonates	Anionic surfactants	HPLC	Determination of toluene, xylene, naphthalene and cumene sulfonic acids. Binary mixture of MeOH-water and MeCN-water were tested as eluents	59
Comparison of different ion sensitive electrodes for the titrimetric determination of ionic surfactants	Ionic surfactant	Titrimetric determination	The behavior of electrode was assessed with regard to their usefulness in routine analysis. The Astec.TSE 01/91 proved to be the most suitable	60
Potentiometric method for determination of nonionic surfactants	Nonionic surfactants	Potentiometric titration	The sample is treated with Dragendorff's reagent followed by measurement of the absorbance of the resulting solution to simplify and accelerate the method and improve selectivity	61

59. M.C.Gutierrer; N.Gago; M.Crespi, Tenside Surfactants, Deterg., 1993, 30(1), 15-17.

60. N.Buschmann, R.Schulz, Teside, Surfactants, Deterg., 1993, 30(1), 18-23.

61. A.N.Drornika; A.A.Fadeer, Tzobreteniya, 1992, (10), 179.

Title	Analyte	Technique	Remarks / Comments	References
Determination of anionic surfactant in waste water by HPLC with a diode array detector	Anionic surfactants	HPLC	Linear alkyl benzene sulfonate and ethoxylated alkyl phenol surfactants were determined in waste water. Determination were made in effluents after filtration and after biological treatment	62
Determination of anionic surfactant in fresh water or in sea water	Anionic surfactants	Solvent extraction and spectrophotometric determination	The extraction of ion pairs with various combinations is desired. Of the dyes and solvents examined ethyl violet and p-xylene are useful combination as the cationic dye and extraction solvent	63
Extraction free determination of cationic surfactant in water by solid phase spectrophotometry	Cationic surfactant	Spectrophotometric method	Determination of surfactant based on the formation of associations of cationic surfactants with cosine and separation by filtration	64

62. R.Schuster, Lab. 2000, 1992, 6(3), 66-67.

63. H.Wu; Hsiung; L.Bijen, J. Chin. Chem. Soc., 1993, 40(1), 29-32.

64. A.T.Pilipenko; A.V.Terletskaya; T.A.Bogoslovskaya, Khim. Tekhnol Vody, 1993, 15(2), 113-120.

Title	Analyte	Technique	Remarks / Comments	References
Analysis of ethoxylated alcohol surfactants in water by HPLC	Surfactants	HPLC	Determination of linear alc. polyethoxylates in water. After extraction of the alcohol ethoxylates into an organic phase ethoxylates are derivatized with Ph isocyanate	65
Test analysis of anionic synthetic surfactants in natural water	Anionic surfactants	Colorimetric method	Determination of the presence of anionic surfactants in waters and sea water. Uses 2,4-diphenyl-8-(4-nitro-3-aminophenyl amino-methylidene)-5,6,7,8-tetrahydrochromyl perchlorate	66
Analysis of surface water active agents by ion exchange chromatography	Ionic and nonionic surfactants	Ion exchange chromatography	Important surfactants were analyzed by ion exchange chromatography for classification in the customs schedule of Japan	67

65. L.Nitschke; L.Huber, Fresenius J. Anal.Chem., 1993, 345(8-9), 585-588.

66. L.V.Boena; V.A.Kimstach; Vinnikova Yu Yu, Gidrkhim, Mater., 1991, 100, 163-167.

67. T. Hirore; A.Takeshi: H.Kasimura, Kanzei Chua Bunsekishoko, 1992, 31, 115-125.

Title	Analyte	Technique	Remarks / Comments	References
Qualitative method for colorimetric determination of surfactant class	Surfactants	Colorimetric and spectrochem analysed	The procedure is accelerated by using a colorimetric reagent comprising a mixture of Lutetium chloride, methyl-thymol blue and cetylpyridium chloride and carrying out the sample treatment in an urotropine buffer pH5	68
Quantitative determination of cationic surfactants in sewage sludges and sediments by super crtical fluid extraction and HPLC applying post column ion pair extraction	Cationic surfactant	Super critical fliuid extraction HPLC, post column ion pair extraction	This determination uses conventional liquid extraction with acidic MeOH followed by purification of the extracts on an anion exchange column and by a sequence of liquid liquid partitioning	69
Tenside analyses by HPLC analysis of anionic and cationic tensides	Anionic and cationic surfactants	HPLC	A review with 24 references anionic and cationic surfactants analysis	70

68. K.Sergej; M.Elena G., Izobreteniya 1992, (14), 183.

69. F.Pilar; A.Alfredo C; G.Walter, Am. Chem.Soc., Div. Environ. Chem. 1993, 33(1), 303-306.

70. L.Nitschki; L.huber, Labor Praxis, 1992, 16(10), 994-996.

Title	Analyte	Technique	Remarks / Comments	References
Determination of nonionic surfactants in detergents, pilot plants baths and rinsing water	Nonionic surfactants	Potentiometric titration	The determination is based on the formation of ternary complex compounds of polyoxy ethylene chains with BaCl and Na tetra phenyl borate. Method apply for determination of various com. surfactants in water	71
Electrochemical properties and analytical capabilities of film electrodes selective to nonionic surfactants	Surfactants like polyethylene glycol (PEG) alkyl phenol ethers (APE)	Electrochemical property	The influence of PEG and APE introduced to the electrode active material, on the electrode properties of the membranes of film electrodes selective to nonionic surfactant. Metal ion transfer at membrane solution boundary and ion transport in the membrane were discussed	72
Determination of nonionic surfactants by spectrophotometry after extraction with potassium tri-iodide	Nonionic surfactants	Spectrophotometry method	The surfactant is extracted into $MeCCl_3$ as an uncharged adducts with KI_3, and the determination is completed by measuring the absorbance of the extraction at 380 nm. The performance of the method in the presence of anionic surfactants and the major ions of anionic sea water is assessed	73

71. K.Vytras; V.Dvorakova, Chemickotechnol Paradubice, 1990, 54, 15-25.

72. R.K.Chernova; E.G.Kulapina; E.A. Materova; E.V.Tretyachenko; A.P.Novikov, Zh. Anal. Khim. 1992, 47(8), 1464-1471.

73. A.A.Boyd-Boland, M.J.Eckert, Anal. Chim Acta, 1993, 271(2), 311-314.

Title	Analyte	Technique	Remarks / Comments	References
Tensido analysis by HPLC analyte of nonionic and ampholytic tensides	Nonionic and ampholytic tensides	HPLC	Reversed phase HPLC for the determination of alkyl chain lengths and normal phase HPLC for the determination of ethoxylate group are discussed	74
Spectrophtometric determination of polyoxyethylated ethers of alkyl phenols in the system bromopyrogallol red-cetypyridinium chloride noionic surfactatnt	Nonionic surfactant	Spectrophtotmetric determination	Nonionic surfactant determined by measuring the decrease of absorbance of the 1:2 bromopyrogallo red-cetylpyridinium ion association at 620 nm	75
Three dimensional phase sensitive ac voltametry; a new experimental approach for the study of phase transition	Anionic surfactants (SDS)	A.C.Voltammetry	It is alternative method for the study of time dependent adsorption processes, one which is especially useful in the case of phase transition choosed SDS as adsorbate	76

74. L.Nitschke; L.huber, Labor Paraxis, 1992, 16 (11), 1114-1116.

75. M.M.Tananaiko; I.L.Gorenshtein, Ukr. Khim. Zh., 1992, 58(2), 177-179.

76. N.Papodopoulos; S. Sotiropoulos; P.Nikitas, NATO ASI Ser., Ser. B, 1992, 290, 199-203.

Title	Analyte	Technique	Remarks / Comments	References
Identification of IR spectra of surfactant	Ionic, nonionic and amphoteric surfactant	IR spectra	A review with 11 references on molecular structures and IR spectra of ionic, nonionic and amphoteric surfactant	77
Cationic surfactant determination in water	Cationic, anionic surfactant	Anion exchange resin (AER) cation exchange resin (CER) spectrometry	Trace amount of cationic surfactant were determined in water by separation with anionic surfactant with anion exchange resin Ambalite TRC 401 concentration with CER Ambalite IRC 84 and elution with a mixture of 1M NaCl and 55% MeOH solution at 50^0 followed by adsorption spectrometry using the orange II method	78
Optimization of analytical conditions for surfactants by HPLC	Surfactant	HPLC	Separation was examined using octadecyl silica as a column packing. C_{16}-C_{18} alkyl benzyl dimethyl ammonium or trimethyl ammonium chloride CPC, benzethonium chloride and distearyl dimethyl ammonium chloride were used as quaternary salts and POE stearyl amine was used as the aliphatic amine	79

77. Q.Zhang; Q.Dai; F.Chen, Riyong Huaxue Gongye, 1992, (2), 95-104.

78. E.Nakamura; H.Namiki, Kogyo Yosui, 1992, 410, 79-83.

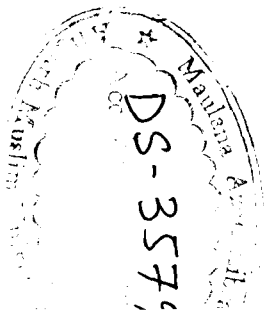
79. H.okumura, J.Secj. 1992, 26(1), 31-38.

Title	Analyte	Technique	Remarks / Comments	References
HPLC separation and quantification of anionic surfactants using a automated online ion pair extraction system	Anionic surfactant	HPLC	The influence of the reagent concentration as well as different sizes and materials of the extraction capillary were evaluated. Calibration curve of surfactant concentration vs fluorescence emission is discussed	80
Determination of trace amount of nonionic surface active agent by HPLC with micro-FTIR using pin-point condensation technique high selectivity detection and HPLC separation method for polyethylene glycol alkyl ether and polyethylene glycol alkyl phenyl ether	Nonionic surfactant	HPLC	The pin-point condensation technique using a perfluorated polymer film on an SUS mirror was applied to solvents eluted from HPLC	81
HPLC analysis of aliphatic ionic surfactans at trace level	Ionic surfactant	HPLC	HPLC separation combined with an online sandwitch type phases separator followed by fluorescence detection, for cationic surfactants normal phase HPLC with 9,10-dimethoxyanthracene-2-sulfonate as the anion resulted in a quantification	82

80. M.Schoester; G.koster, Fresenius J. Anal.Chem. 1993, 345(12), 767-772.

81. S.Iso; T.Nakamura; H.Uchihara; M.Ikada, Kankyo Kagaku, 1993, 3(2), 231-237.

82. G.Kloster; M.Schoster; S.Milan J., Comun. Journ. Com. Esp. Detrg. 1993, 24, 25-33.



Title	Analyte	Technique	Remarks / Comments	References
Method for determining anionic surfactants by potentiometric titration	Anionic surfactant	Potentiometric titration	To increase the sensitivity and selectivity of the method and expand the raw material base, the membrane contains, as the electrode active substance, a complex salt of lauryl sulfate or dodecyl benzene sulfonate and dye methylene blue	83
Visual colorimetric determination of anionic surfactants in synthetic materials	Anionic surfactant	Visual colorimetric determination	The chloroform extraction of a synthetic material is treated with methylene blue or thymol blue end after layer separation color is compared to standard solutions	84
Characterization of CPC on HPTLC plates by microsurface enhanced Raman Scattering	Cationic surfactant	HPTLC and micro surface enhanced Raman scattering (micro-SERS)	The technique was used for in situ study of the adsorption behavior of CPC on silica gel. SERS is powerful technique monitoring the behavior of CS for assessing adsorbate orientation and conformation for proling the effect of various environmental factors an interaction between the adsorbate silica gel-Ag colloid substrate	85

83. M.Lyadmila I.; M.Isanna L.; V.Svethana P., Izobreteniya, 1992, (44), 146.

84. P.I.Selivokhim, Kozh-obuvn. Prom-st, 1992, (4), 35.

85. E.Koglin, J. Planar Chromatogr.-mod. TLC, 1993, 6(1), 88-92.

Title	Analyte	Technique	Remarks / Comments	References
Use of differential pulse polarography and adsorption stripping tensammetry for investigation of gas stripping separation of nonionic surfactants	Nonionic surfactant	Polarogrphy and adsorptive stripping tensammetry	Determination of surfactants in surface and waste water	86
Methods for surfactant micro analysis	Surfactant	HPLC and mass spectrometer	Microanalysing the ionized surfactant with a mass spectrometer. Deuterium labeled C_{12}&C_{14} alkyl sodium sulfate were prepared and used for microanalysis of C_{12}&C_{14} surfactants	87
Determination of SDS using several internal standards by multivariate analysis of Curie point, pyrolysis gas chromatography	Anionic surfactant	Multivariate analysis	Multivariate applied to quantitative analysis of SDS by pyrolysis gas chromatography	88

86. Z.Lukaszewski; A.Szymanski; B.wyrwas, Fenzi Ceshi Tongbao, 1992, 11(3), 9-12.

87. N.Kondo; H.Tokudo; K.Matsumoto, Jp Appl. 1993, 91, 168.

88. M.Hida; S.Okuyama; T. Mitsui; Y.Minami; Y. Fujimura, Chromatographia 1993, 35, 643-648.

Title	Analyte	Technique	Remarks / Comments	References
Solvent strength and selectivity in TLC separation of ethylene oxide oligomers	Nonionic tenside	TLC	Separation of various nonionic tenside consisting of ethylene oxide oligomer mixtures. Solvent strength and selectivity were calculated. Selectivity is higher on alumina than on silica gel	89
Analytical study of highly condensed nonionic surfactants separation on cation exchanges	Nonionic surfactants	Cation exchange	The influence of the nature of cations on the separation of selectivity is examined including alkali earth metals, transition and quaternary ammonium ions as well as proton	90

89. T.Cserhati, J. Chromatogr. Sci., 1993, 31(6), 220-224.

90. B.Desmazieres; F.Portet; P.L.Desbene, Chromatographia, 1993, 36, 307-317.

Title	Analyte	Technique	Remarks / Comments	References
HPLC determination of cationic and amphoteric surfactants in cosmetics	Cationic and amphoteric surfactant	HPLC	An aqueous methanol solution containing glycine-perchloric acid salt was used as a mobile phase. The ion exchange mechanism was confirmed to be operative in this separation	91
Analysis of surfactants by ion chromatography	Surfactant	Ion chromatography	A review with references on the development of ion chromatographic techniques in the analysis of surfactants	92
Improvement of ethyl violet method for Spectrophotometric determination of anionic surfactants	Anionic surfactant	Spectrophotometric determination	Trace amounts of SDS were determined in water by addition of a mixture of 1M Na_2SO_4 and 1mM Et violet (I) at pH 5 extraction with PhMe and washing with a mixture of 1.5 μMI and 1% Na_2SO_4 solution followed by adsorption spectrometry	93

91. M.Matsuzaki; K.Ishii; H.Yoshimura; S.Hashimoto, J. Secj, 1993, 27(2), 494-497.

92. Y.Zhu; J. Chen; S.Xu, HuaxueShijie, 1992, 33(11), 511-512.

93. E.Nakamura; N.Tsuyuzaki; H.Namaki, Kogyo Yosui, 1993, 421, 21-25.

Title	Analyte	Technique	Remarks / Comments	References
Separation of different types of surfactants by thin layer chromatography	Surfactants	TLC	The separation of different types of surfactants has been achieved by multiple development on silica plates	94
Paper adsorption Spectrophotometric determination of anionic surfactant in environmental water by methylene blue method	Anionic surfactant	Spectrophotometric	System detd. Absorbance at 670nm and 730 nm with spectrophotometer. System obeys Beer's Law. Anionic surfactants pptd with methylene blue	95
Spectrophotometric determination of anionic surfactants in water using Victoria Blue B	Anionic surfactant	Spectrophotometric	Victoria blue B reacts with dodecyl benzene sodium sulfonates in the presence of gelatin and H_2SO_4 to form a blue color stable complex. The recovery rate of standard matter is 94.5 – 99.1%	96

94. A.Kruse; N.Buschmann; N.Cammann, J. Planar. Chromatogr.-mod TLC, 1994, 7(1), 22-24.

95. Ma.Degjum; Li Liging, H.Daxue Xuebow; Ziran Kexueban, 1993, 13(2), 40-44.

96. H.Guan; J.Zhang, Taiyurn Gongye Daxue Xubao, 1993, 24(4), 55-58.

Title	Analyte	Technique	Remarks / Comments	References
The use of differential pulse and dc polarography in the analysis of solutions containing surfactants	Surfactants	Polarography	Effects of surfactants on DPP curves were demonstrated for 4-nitro benzoic acid in the presence of oligomers resulting from washing lignin preparations with water	97
Selective electrodes for differential determination of anionic and nonionic surfactants	Anionic and nonionic surfactant	Uses selective electrode	A selective electrode with a mixed membrane enables separative determination of nonionic and anionic surfactants in the presence of each other. Method developed for the analysis of synthetic detergents	98
Environmental analysis with a simple and low cost colorimeter	Ionic surfactants	Colorimeter	A hand made colorimeter consist of a black cylindrical film case, Cs photocall, red and green LEDs and wheat stone bridge circuit and an optical cell. Analysis of PO_4^{3-} and ionic surfactants in river waters	99
Determination of ionic and nonionic surfactants by HPLC	Ionic and nonionic surfactants	HPLC	Study the degree and kinetics of biodegradation of surfactants	100

97. E.Rupp; P.Zuman, Anal. Lett., 1994, 27(5), 939-955.

98. R.K.Chernova; E.A.Materova; E.A.Tretyachenko; A.Z.kulapin, Zh. Anal. Khim, 1993, 48(10), 1648-1652.

99. H.Ekawa, Kagaku to Kyoiku, 1993, 41(11), 762-765.

100. L.Nitschke, Deterg., 1993, 30(6), 413-416.

Title	Analyte	Technique	Remarks / Comments	References
Determination of dihardened tallow dimethyl ammonium compounds (DHTDMAC) in environmental matrixes using trace enrichment techniques and HPLC with conductometric detection	Dihardened tallow dimethyl ammonium compounds	Trace enrichment conductometric and HPLC	Determination of very low concentrations (down to ppb) of DHTDMAC, major cationic surfactants, in a range of environmental matrixes. HPLC gives accurate and reproducible results	101
Determination of anionic, cationic and nonionic surfactants by HPLC	Ionic and nonionic	HPLC	The content of single surfactants in mixtures of surfactants, to drive information about surfactant structure	102
Studies on analysis of emulsifiers systematic analysis of ester type nonionic surfactants	Nonionic surfactants	HPLC with UV detector and refractive index determination	Studies on analysis of emulsifiers systematic analysis of ester type nonionic surfactants	103

101. P.Gerike; H.Klotz; J.G.A.kooijman; E.Matthyjis; J.Waters, Water Res., 1994, 28(11), 147-154.

102. L.Nitschke, Tenside, Surfactants, Deterg., 1993, 30(6), 413-416.

103. E.Takagi; K.Wakabayashi; H.Ohtani; M.Kanov, J. Secj, 1993, 27(1), 48-53.

Title	Analyte	Technique	Remarks / Comments	References
An automated method for determination of anionic surfactants in personal care products	Anionic surafctants	Automated titration	Automated titration for the determination of anionic surfactants in shampoos and tooth pastes	104
Analyses of polyethoxylated nonyl phenols by supercritical fluid chromatography and HPLC	Surfactant eg. Polyethoxylated nonyl phenols	HPLC and SFC	Analyses of polyethoxylated nonyl phenols by supercritical fluid chromatography and HPLC	105
Analysis of nonionics and alcohol ethoxylated. Application of confirmatory biodegradation test effluents	Nonionic surfactants	HPLC FTHNMR analysis	HPLC method is able to determine the content of alcoholic ethoxylates. This paper describes a nonspecific analytical procedure to evaluate total nonionic surfactants and specific HPLC determination of alcoholic ethoxylates in water	106

104. C.Denis H. Am Lab., 1993, 25(150, 44.

105. Z.Wang; M.Fingas, J. Chromatogr.Sci., 1993, 31(12), 509-518.

106. L.Cavalli; A.Gellira; G.Cassani; M.Lazzrin; C. Maraschin; G.Nucci, Sostanze Grasse, 1993, 70(9), 447-452.

Title	Analyte	Technique	Remarks / Comments	References
Analysis of Sorbiton ester surfactants Part I : HPLC	Ester surfactants	HPLC	Reversed HPLC employing C18 column was developed for rapid separation of sorbitan ester surfactants and the quantitative determination of the distribution of sorbitan mono, di-, tri- and tetra esta fractions	107
Photometric titration of small amounts of cationic surfactants in an aqueous medium	Cationic surfactant	Photometric titration	Direct or indirect titrations for the determination of cationic surfactants were examined. Dodecyl benzene sulfonates (DBS) was used as titrant for cationic surfactant indirect titration. Photometric titration for (CS) with tetrabromo phenolphthalein Et ester as an indicator	108
Analysis of nonionic surfactants using solid phase extraction combined with super critical fluid extraction and chromatography	Nonionic surfactants	Solid phase extraction and super critical fluid extraction chromatography	Determination of nonionic surfactants in water uses solid phase extraction disks as a pre extraction step in combination with super critical extraction and chromatography	109

107. Z.Wang; M.Fingas, J. High Resolut. Chromatogr., 1994, 17(1), 15-19.

108. S. Motomizu; G.Yun-hua; K.Uemura; S.Ishihara, Analyst., 1994, 119(3)

109. M.Kane; J.R.Dean; S.M.Hitcheri; C.J.Dowle; R.L.Tranter, Anal. Proc. 1993, 30(10), 399-400.

Title	Analyte	Technique	Remarks / Comments	References
Direct determination of nonionic surfactants in spiked tap water by desorption chemical ionization and tandom mass spectrometry	Nonionic surfactant	Mass spectrometry	A mass spectrometric method employing desorption ionization has been set up to analyze nonionic surfactant mixtures. Method is sufficiently sensitive to work with detection limits placed in the low ppm range	110
Extraction photometric determination of nonionic synthetic surfactants in water	Nonionic surfactants	Photometric determination	Procedure for the determination of nonionic synthetic surface active substances in natural and waster water	111
Flow injection method coupled with solvent extraction using on tube visible absorption and application to the determination of anionic surfactant	Anionic surfactant	Flow injection, solvent extraction and visible absorption	Determination of anionic surfactants by flow injection Spectrophotometric method using solvent extraction / ontube visible detection	112

110. M.Vincenti; C.Minero; E.Pellizzeti, Ann. Chim., 1993, 83(9-10), 381-396.

111. L.V.Boeva; I. N.Urazova; V.Yu Ya, Zh. Anal.Khim., 1994, 49(4), 381-384.

112. S.Motomizu; M.Oshima; N.Goto, J. Flow injection Anal., 1993, 10(2), 255-261.

Title	Analyte	Technique	Remarks / Comments	References
Determination of nonionic surfactants inriver water and waste water by X-ray fluorescence spectrometry (XRFS), atomic absorption spectrometry (AAS) and polarography	Nonionic surfactant	(XRFS), (AAS) and polarography	Trace nonionic surfactants (100-1000μg/500cm^3) concentrations were detected in river water and waste water using XRFS, AAS and polarography. Triton X-100 was used as the refernce compound	113
Indirect determination of surfactants by adsorptive voltametry Part 2. determination of hexa diacyl trimethyl ammonium bromide and cetyl pyridinium chloride in industrial and consumer products	Cationic surfactants	Adsorptive voltametry	Determination of hexadiacyltrimethyl ammonium chloride in industrial and consumer products	114
Mass spectrometric identification of anionic surfactants in two chemical additives	Anionic surfactants	Mass spectrometry	Mass spectrometry was used for the identification of anionic surfactants in two chemical additives	115

113. W.Winkler; F.bull, Przem. Chem., 1994, 73(8), 314-315.

114. S.B.Adeloju; S.J.Shaw, Electroanalysis , 1994, 6(8), 645-649.

115. Y.Zuo; X.Xu; F.Ni; E.Qi, fenxi Ceshi Xuebao, 1994, 13(5), 10-14.

Title	Analyte	Technique	Remarks / Comments	References
Determination of chain length distribution of anionic surfactants. Use of high resolution capillary gas chromatography (HRCGC) in the determination of chain length distribution of anionic surfactants	Anionic surfactants	High resolution capillary gas chromatography (HRCGC)	Determination of chain length distribution of anionic surfactants. Use of high resolution capillary gas chromatography (HRCGC) in the determination of chain length distribution of anionic surfactants	116
Separation and detection of alkylpolyglucosides in HPLC	Alkylpolyglucosides	Reversed phase HPLC	Alkylpolyglucosides were separated by reversed phase HPLC and two detection methods were tested. Evaporative light scattering detection and electrochemical detection at a gold electrode	117
Determination of amphoteric surfactants in cosmetic cleansing products by high performance liquid chromatography on a cation exchange column	Amphoteric surfactants	HPLC	Amphoteric surfactants in cosmetic cleansing products by HPLC on a cation exchange column	118
Quantitative analysis of pulmonary surfactant phospholipids by HPLC and light scattering	Pulmonary surfactant phospholipids	HPLC	Quantitative analysis of pulmonary surfactant phospholipids by HPLC and light scattering	119

116. D.Louis; J.M.Talbot, Tenside, Surfactants Deterg., 1995, 32(4), 347-350.

117. H.Paul R; H.Anthony; B.Wolfgang, J. Chromatogr. A 1995, 706(1+2), 571-578.

118. A.Tegler; W.Ruess; E.Gmahl, J. Chromatogr. A 1995, 715(1), 195-198.

119. H.Buegner; U.Pison, J. Chromatogr. B; Biomed Appl., 1995, 672(1), 25-31.

Title	Analyte	Technique	Remarks / Comments	References
Ion selective electrodes for determination of ionogenic and nonionogenic surface active substances	Ionogenic and nonionogenic surface active substances	Ion selective electrodes	Ion selective electrodes for determination of ionogenic and nonionogenic surface active substances	120
Separation of anionic surfactants on anion exchanger	Anionic surfactants	Anionic exchanger	Anion exchanger is used for separation of anionic surfactants	121
Separation of octyl phenol poly ether alcohol surfactants by capillary column SFC and HPLC	Octyl phenol poly ether alcohol	Capillary column SFC and HPLC	Separation of octyl phenol poly ether alcohol surfactants by capillary column SFC and HPLC	122
Volumetric method for determining surface active substances in liquid media	Surface active substances	Volumetric method	Surface active substances was determined by using volumetric method	123

120. E.Yu.Khmelmitokoya; I.V.Garbanova; B.N. Kolokov, Zavod. Lab., 1995, 61(6), 4-7.

121. N.Pan; D.Donald J. J. Liq.Chromatogr. A 1995, 706(1+2), 327-337.

122. Ye. M.Ye; W.Ron G; H.Kim D., J. Liq. Chromatogr. 1995, 18(12), 2309-2322.

123. K.Yurij A.; K.Elena I.; K.Tatyana I. Izobreteniya 1993, (37-38), 181-182.

Title	Analyte	Technique	Remarks / Comments	References
Chromatography of cationic surfactants : HPLC, TLC and GC	Cationic surfactants	HPLC, TLC and GC	A review with 89 references on analysis of cationic surfactants with HPLC, TLC and GC	124
Analytical methods of alkylpolyglycosides	Alkylpolyglycosides (APG)	TLC	APG with different alkyl chain length are separated by TLC on RP_{18} with MeOH/water 9:1 (vol.) and visualized by spraying with dilute H_2SO_4 and heating	125
Relationship between hydrophile lopophile balance and behavior in reversed phase thin layer chromatography of some nonionic surfactants	Nonionic surfactants	TLC	An equation was derived to establish the HLB values of polyethoxylated nonionic surfactants (Brij and Triton X series) from TLC parameters	126

124. P.B.Mepherson; R.Henvik T., surfactant Science Series 1994, 53, 289-326.

125. S.Wardarczak; N.Bushmann, GIT Frachz Lab. 1995, 39(5), 410-412.

126. C.Attomare; G.Trapani; M.franco; A.Latrofa; G. Liso, Acta Technol. Legis Med., 1995, 6(1), 33-41.

Title	Analyte	Technique	Remarks / Comments	References
Comparison of chromatographic behavior of oligoethylene glycol nonylphenol ether nonionic and anionic surfactants in reversed phase HPLC	Anionic and nonionic surfactants	Reversed phase HPLC	Comparison of chromatographic behavior of oligoethylene glycol nonylphenol ether nonionic and anionic surfactants in reversed phase HPLC	127
Mass spectrometry of cationic surfactants	Cationic surfactants	Mass spectrometry	A review with 89 references on the mass spectrometry techniques for analysis of cationic surfactants	128
Ion selective electrode for determination of surfactants	Surfactants	Ion selective electrode	Use of ion selective electrodes for determination of surfactants	129
Determination of adsorbed nonionic surfactants on fabrics by HPLC	Nonionic surfactants	HPLC	Determines the adsorbed nonionic surfactants on fabrics	130

127. P.Jandera; J.Urbanck, J.Chromatogr. A 1995, 689(2), 255-267.

128. K.Kalons; T.Henry, Surfactant Sci. Ser., 1994, 53, 257-288.

129. C.Rimma K.; K.Elena G.; M.Elena A.; T.Elena V.; B.Olga V.; N. Lyudkila V.; S.Irinak, Izobreteniya 1993, (14), 177.

130. V.Bosdorf; T. Bluhm; H.Kruessmann, Text. Prax. Inst., 1994, 49(5), 348-350, 353-354.

Title	Analyte	Technique	Remarks / Comments	References
Spectrophotometric determination of anionic surfactants in natural water with bromophenol blue and cetylpyridine chloride	Anionic surfactants	Spectrophotometry	A method for the spectrophotometric determination of anionic surfactants with bromophenol blue and cetylpyridine chloride was developed	131
Two indicator two phase titration for polyoxyethylated carboxylates and other anionic surfactants	Anionic surfactants	Two indicator two phase titration	In this method, hexadecylpyridinium was used as the titrant with saframine and methylene blue as the indicator and chloroform as the solvent for phase separation	132
Retention behavior of nonylphenol ethylene oxide oligomers on alumina column	Nonylphenol ethylene oligomers	HPLC	Nonylphenol ethylene oxide oligomers have been separated by HPLC on alumina columns with Et. Acetate/n-hexane mixtures as eluents	133
Analysis of surface active agents; as environmental pollutants	Surface active agents	--	A review with 89 references on the determination of anionic, cationic and nonionic surfactants in the environment	134

131. H.Fan; X.Yi; G.Hu, Fenxi Huaxue 1994, 22(10), 1051-1053.

132. Liu. Yun, huaxue Shiji, 1994, 16(6), 365-367.

133. E.Fargacs; T.Cserhati, Fresenius J. Anal. Chem., 1995, 351(7), 688-689.

134. I.Kobayashi, Bunseki 1995, (2), 123-128.

Title	Analyte	Technique	Remarks / Comments	References
Spectrophotometric determination of sodium dodecyl sulfate based on ion pair extraction with copper (I), 1.10-phenanthroline complex	Sodium dodecyl sulfate	Spectrophotometry	The method was based on the formation of the SDS-[Cu(II)-1,10-phenanthroline] ion pair and extraction into iso-BuMeketone (MiBK)	135
Quantification of sodium dodecyl sulfate in a two phase system using filament pulse pyrolysis gas chromatography	SDS	Filament pulse pyrolysis gas chromatography	Determination of SDS in the presence of a charged water – sol polymer is presented	136
Ion chromatographic characterization of ethoxylated anionic surfactants	Ethoxylated anionic surfactants	Ion exchange chromatography	A method for the characterization of ethoylated anionic surfactants	137
Extraction fluorometric determination of cationic surfactants using 3,5-dibromo slicylaldehyde-thiosemicarbazone	Cationic surfactants	Extraction fluorometry	Extraction fluorometric determination of cationic surfactants using 3,5-dibromo slicylaldehyde-thiosemicarbazone	138

135. M.Morita; T.kamidata; H.Watanabe, Yukayaku, 1995, 44(2), 145-147.

136. P.Almen; I.Ericsson, Langmuir 1995, 11(1), 108-110.

137. A.Stemp; A.V.Boriraj; P.Neill, J. Am. Oil. Chem. Soc., 1995, 72(1), 17-22.

138. Z.Y.C.Yang; C.Zhang, Huaxue Shiji 1994, 16(5), 271-271.

Title	Analyte	Technique	Remarks / Comments	References
Determination of sunscreen agents by micellar electrokinetic chromatography	Sunscreen agents	Micellar electrokinetic chromatography	Determination of sunscreen agents by micellar electrokinetic chromatography	139
Analysis of nonionic surfactants by HPLC using evaporation light scattering detector	Nonionic surfactants	HPLC with evaporation scattering detector	An evaporative light scattering detector was used to select chromatographic conditions that characterize the majority of nonionic surfactants	140
New reagent for extraction photometric determination of anionic surfactants	Anionic surfactants	Extraction photometry	A new reagent 2,6-diphenyl-4-(4-dimethylamino)styryl pyridinium chloride is proposed for extraction of photometric determination of anionic surfactants	141
Application of ac polarography and voltametry for determination of surface active substances	Surface active substances	AC polarography and voltametry	AC polarography and voltametry are used for determination of surface active substances	142

139. P.G.Pietta; A.Bruno; P.L.Mauri; C.Gardana; R.Mattei-Facino; M.carini, J. Pharm. Biomed. Anal., 1995, 13(2), 229-235.

140. N.Martin, J. Liq. Chromatogr., 1995, 18(6), 1173-1194.

141. R.K.Chemova; N.I.Yastrebova; N.Pankratov, Zavod Lab. 1994, 60(8), 4-6.

142. B.Csovic, Kem. Ind., 1994, 43(12), 497-502.

Title	Analyte	Technique	Remarks / Comments	References
Ion selective electrode for determination of the concentration of nonionic surfactants	Nonionic surfactants	Ion selective elctrode	Ion selective electrode is used for determination of the concentration of nonionic surfactants	143
Analytical methods for carbohydrate surfactants	Carbohydrate surfactants	TLC and spectrophotometry	This paper describes two analytical methods for a fast, simple and reliable analysis of alkyl polyglucosides	144
A comment on the use of colorimetric and HPLC determinations of nonionic surfactants in river water	Nonionic surfactants	Colorimetry and HPLC	Nonionic surfactants were determined in river water to compare environmentally useful information obtainable using a non specific colorimetric method and HPLC	145
The identification of anionic detergents by thin layer chromatography	Anionic surfactants	TLC	Anionic surfactants were identified by TLC on silica gel plates using BuOH-HOAc-isoPrOH (3.1:0.3) solvent system and azure A and dragendorff reagent for their vizualization	146

143. H-U. Dammer, Tenside, Surfactants Deterg., 1995, 32(1), 12-16.

144. N.Buschmann; S.Woderczark; Comun. Jorn. Con. Esp. Deterg. 1994, 25, 203-207.

145. V.Zelano; D.Gastaldi; G.Ostacoli; F.Siviero; A.Torazzo, Ann. Chim. 1994, 84(11-12), 521-528.

146. S.Akinci; G.Kasim C., Acta Pharm. Turc., 1992, 34(4), 121-126.

Title	Analyte	Technique	Remarks / Comments	References
Separation of fatty components by solid phase adsorption Part II. Determination of fatty substrates in fat liquoring baths other applications	--	TLC	The method was used for analysis of fat liquoring baths from natural and synthetic fats	147
Lipophilicity determination of non homologues series of nonionic surfactants by TLC	Nonionic surfactants	Reversed phase TLC	The lipophilicity and specific hydrophobic surface area of 22 nonionic surfactants, having different hydrophobic moieties have been detected	148
Identification of narrow distribution lauryl alcohol ethoxylate by TLC	Lauryl alcohol ethocylates	TLC	The compn. of polyethylene glycol lauryl ether nonionic surfactantwas analised by TLC in EtOH solution on a silica gel plate using 55:35:10 EtOH-acetone-water mixtures	149

147. J.Cot; M.Fort; J.Cartiel, AQEIC Bol Tec, 1992, 43(4), 147-157, 162-167.

148. J.Cserhati, J. Biochem. Biophysics Methods, 1993, 27(2), 133-142.

149. Wu. Zhining, Riyong Huaxue Gongye, 1992, 3, 149-154.

Title	Analyte	Technique	Remarks / Comments	References
Characterization of polyethylene glycerol trioleate, a nonionic surfactant by TLC	Polyethylene glycerol trioleate	TLC	A sensitive, specific and reproducible TLC method was developed for separation of the oligomers of Tagat TO, a polyoxyethylene glycerol trioleate nonionic surfactant	150
Alkyl polyglycosides (APG) analysis of raw material determination in products and environmental matrixes	APG	High temperature gas chromatography, HPLC and TLC	HTGC, HPLC and TLC are presented for the characterization of alkyl polyglycosides raw material for surfactants	151
Titrimetric analysis of ionic surfactants	Anionic surfactants	Potentiometric titration	The potentiometric titration of anionic surfactants is a good alternative to the two phase titration for a wide variety of applications	152

150. M.Rischer; I.behr; E.Wolf-Henss; J.Engel, J. planar Chromatogr. Mod. TLC 1995, 8(5), 382-387.

151. H.waldoff; J.Scherler; M.Schmitt, World Surfactants Congr. 4th 1996, 1, 507-518.

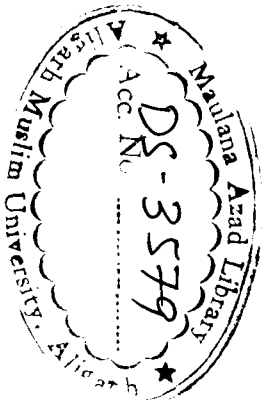
152. N.Buschmann, tenside, Surfactants, deterg. 1995, 32(6), 504-506.

Title	Analyte	Technique	Remarks / Comments	References
Ethyl violet method for Spectrophotometric determination of anionic surfactants in environmental water	Anionic surfactant	Spectrophotometry	Anionic surfactant were extracted from water with ethyl violet toluene, the organic phase was subjected to the absorptive spectrometry at a wavelength of 611 nm	153
Determination of anionic surfactant in water	Anionic surfactants	Two phase titration	The concentration of various types of anionic surfactants in water and waste water were detected by two phase titration using azophotoxine as indicator benzyoxyphenyl chloride as tittrant	154
Spectrophotometric determination of cationic surfactants based on Iron (III) chrome azurol S complex	Cationic surfactants	Spectrophotometry	An extraction free Spectrophotometric method is proposed which is based on the formation of ternary complexes with Iron (III) and chrome Azurol S	155

153. A.kiyoko; A.timura; H.Ogura, Chiba-ken Swshitsu Hozen kenkyusho Nenpo 1994, 79-82.

154. Weiguo; H.Zhu, Huanjing Kexue 1995, 16(2), 59-62.

155. M.Song; R.ShuQuan, Chin. Chem. Lett, 1995, 6(11), 979-982.



Title	Analyte	Technique	Remarks / Comments	References
Determination of alkylated and sulfonated diphenyl oxide surfactants by high performance liquid chromatography	Alkylated and sulfonated diphenyl oxide surfactants	HPLC	The separation of 11 components in Dowfax 8390 is achieved using gradient reverse phase chromatography	156
Separation and characterization of surfactants by high performance thin layer chromatography	Surfactant	HPTLC	The separation of different types of surfactants of all four types has been achieved by single development on silica plates	157
Titrimetric determination of anionic surfactants in an aqueous micellar medium of a non ionic surfactant	Anionic surfactants	Titrimetry	An extraction free titrimetric determination of anionic surfactants in the nonionic surfactant media is presented	158

156. M.Ye; R.Walkup; K.hill, J. Liq. Chrometogr. Relat. Technol., 1996, 19(8), 1229-1240.

157. S.Simuric; Z.Soljic, J. Liq. Chrometogr. Relat. Technol., 1996, 19(7), 1139-1149.

158. S.A.Kulichenko; V.V.Sukhan, Zarod. Lab. 1995, 61(12), 11-13.

Title	Analyte	Technique	Remarks / Comments	References
Determination of anionic detergents in water by high performance liquid chromatographic method	Anionic surfactant	Adsorption preconcentration	An effect of anomalous retention of the ion pair of anionic surfactants with cationic dye on a extraction chromatographic column with chloroform was found	159
Determination of anionic detergent in water by high performance liquid chromatographic method	Anionic detergent	HPLC	A HPLC method to determine linear alkylbenzene sulfonates (LAS) in water was studied	160
Determination of alkylphenols and linear alkylbenzene sulfonates in sediments applying accelerated solvent extraction (ASE)	Anionic surfactants	ASE	Determination of alkylphenols and linear alkylbenzene sulfonates in sediments applying accelerated solvent extraction (ASE)	161

159. L.N.Moskvin; D.N.Nikoleava; N.V.Mikhailova, J. Anal. Chem., 1996, 51(3), 282-285.

160. M.Zhang; Y.Wang; W.Liu, Shanghai Huanjing Kexue 1995, 14(8), 29-31.

161. K.Andrea; D.Hans-Werner, Fresenius J. Anal. Chem., 1996, 354(7-8), 921-924.

Title	Analyte	Technique	Remarks / Comments	References
Analysis of technical poly(ethylene oxides) by online HPLC/H-NMR	Poly(ethylene oxides)	HPLC/H-NMR	Online HPLC/H-NMR is used for analysis of poly(ethylene oxides)	162
Recent advances in the analysis of highly ethoxylated alkyl phenol surfactants	Ethoxylated alkyl phenol surfactants	GC, HPLC and High Performance size exchange chromatography	A review with 40 references on the determination of the degree of the ethoxylation of ethoxylated alkylphenol surfactants by GC, HPLC and high performance size exchange chromatography	163
Spectrophotometric study on color reaction of anionic surfactant with dodecyldimethyl benzylammonium bromide and bromothymol blue	Anionic surfactants	Spectrophotometry	Spectrophotometruic study on color reaction of anionic surfactant with dodecyldimethyl benzylammonium bromide and bromothymol blue	164

162. H.Pasch; W.Hiller, Macromolecules 1996, 29(20), 6556-6559.

163. F.Ysambertt; N.Marquez; A.Gracia, J.Lachaise; J-L.Salager, 4th 1996, 4, 110-121.

164. Y.Wang; G.Li; C.Liu; C.Lu, Fenxi Shiyanshi 1996, 15(2), 53-55.

Title	Analyte	Technique	Remarks / Comments	References
Characterization of quaternarized truethanolamine esters (esterquats) by HPLC, HRCGC and NMR	Quaternarized truethanolamine esters	HPLC, HRCGC and NMR	Characterization of quaternarized truethanolamine esters (esterquats) by HPLC, HRCGC and NMR	165
Spectrophotometric determination of surfactants with bromophenol blue and bromopyrogallol red	Cationic surfactant	Spectrophotometry	The results investigating association reaction of cationic surfactants with sulfophthalein dyes bromophenol blue and bromopyrogallol red and their metal complexes with metal ions in aqueous solutions	166
Spectrophotometric determination of cationic surfactants by formation of ternary complexes with Fe(III) and chrome azurol	Cationic surfactants	Spectrophotometry	Spectrophotometric determination of cationic surfactants by formation of ternary complexes with Fe(III) and chrome azurol	167

165. A.J.Wilkes; C.Jacobs; G.Walraven; M.J.Talbot, World Surfactants congr. 4th 1996, 1, 389-402.

166. L.I.Gorenshtein; M.M.Tananiko; V.V.Sukhan, Ukr. Khim. Zh. 1995, 61(7-8), 31-34.

167. M.Song;L.Shu-Quan, Chin. J.Chem, 1996, 14(3), 228-234.

Title	Analyte	Technique	Remarks / Comments	References
Capillary electrophoresis of cationic surfactants with tetrazolium violet and of anionic surfactants with adenosine monophosphate and indirect photometric detection	Cationic and anionic surfactants	Capillary electrophoresis with indirect photometric detection	Capillary electrophoresis of cationic surfactants with tetrazolium violet and of anionic surfactants with adenosine monophosphate and indirect photometric detection	168
Thin layer chromatographic behavior of substrate and products from the synthesis of Gemini type surface active agents	Gemini type surface active agents	TLC	Silica gel G and acetone benzene were used as stationary and mobile phases chromic acid a mixture of cobalt(II)nitrate and potassium thiocyanate were used for detection	169
Spectrophotometric determination of anionic surfactants in water with bromocresol green and cetylpyridinium bromide	Anionic surfactants	Spectrophotometry	Spectrophotometric determination of anionic surfactants in water with bromocresol green and cetylpyridinium bromide	170

168. S.Shadab A.; D.Neil D, J.Chromatogr. A 1996, 739(1+2), 405-412.

169. I.Baranowska; E.Zielinski: E.Lekawska: B.Kozielska, J.Planar chromatogr-mod. TLC 1996, 9(3), 189-191.

170. Y.Wang; G.Li; Z.Liu; C.Lu, Huanjing kexue 1996, 17(1), 75-77.

Title	Analyte	Technique	Remarks / Comments	References
Analysis of cationic surfactants in household products by high performance liquid chromatography with nitrogen chemiluminescence detection	Surfactants	HPLC with nitrogen chemiluminiscence detection	HPLC with nitrogen chemiluminiscence detection for the analysis of cationic surfactants is described	171
Oligomeric separation of ionic and nonionic ethoxylated polymers by capillary gel electrophoresis	Ionic and nonionic surfactants	Capillary gel elctrophoresis	Capillary gel elctrophoresis used for the oligomeric separation of ionic and nonionic ethoxylated polymers is described	172
Alkyl plyglycosides (APG) analysis of raw materials; determination in products and environmental samples	APG	HTGC, HPLC and TLC	Analytical methods which were developed for APG characterization and detection are presented	173

171. J.Truchan; T.H.Rasmussen; O.Nicolas; Mcpherson; P.bruce, J. Liq. Chromatogr. Relat. Technol. 1996, 19(11), 1785-1792.

172. R.A.Wallingford, Anal.Chem., 1996, 68(15), 2541-2548.

173. H.Waldhoff; J.Scherler; M.Schmitt, World SurfactantS congr. 4th 1996, 1, 507-518.

Title	Analyte	Technique	Remarks / Comments	References
Qualitative trace analysis of surfactant mixtures by reversed phase high performance liquid chromatography with refractometric detection	Surfactants	HPLC with refractometric detection	HPLC with refractometric detection is used for qualitative trace analysis of surfactant mixtures	174
Nonionic surfactant polarity index determination by inverse gas chromatography	Nonionic surfactants	Inverse gas chromatography	The little technique is used to characterize nonionic surfactants	175
RPLC analysis of alkyl polyethylene glycol ethers using evaporative light scattering detection	Alkyl polyethylene glycol ethers	RPLC with light scattering detection	RPLC with light scattering detection is used for the analysis of alkyl polyethylene glycol ethers	176
Identification and quantification of surfactants in consumer products by ion spray mass spectrometry	Surfactants	Ion spray mass spectrometry	Ion spray mass spectrometry is used for identification and quantification of surfactants	177

174. P.L.Desbene; F.I.Portet; G.L.Goussot, J. Chromatogr. A, 1996, 730(1+2), 209-218.

175. M.W.Edens; V.M.Nare; J.C.Knoell, Polym. Mater. Sci., 1993, 69, 551-552.

176. F.Guerreno; J.L.Roccu, Chin. Oggi, 1995, 13(4-5), 11-15.

177. I.Ogura; D.L.Duval; S.Kawakami; K.Miyajima, J.Am.Oil Chem.Soc., 1996, 73(10, 137-142.

Title	Analyte	Technique	Remarks / Comments	References
Determination of surfactants in surface water by solid phase extraction, liquid chromatography-mass spectrometry	Surfactants	Solid phase extraction, liquid chromatography-mass spectrometry	Determination of surfactants in surface water by solid phase extraction, liquid chromatography-mass spectrometry is discussed	178
Titration of ionic surfactants	Ionic surfactants	Potentiometric titration	A method for Potentiometric titration of ionic surfactants using surfactants using surfactant sensitive electrodes is described	179
Capillary electrophoresis of phosphate ester surfactants with adenosine monophosphate and indirect photometric detection	Ester surfactants	Capillary electrophoresis	Capillary electrophoresis of phosphate ester surfactants with adenosine monophosphate and indirect photometric detection	180

178. S.Simon; D.C.Malcolm; C.Michael; A.Alison, J. Chromatogr., A 1996, 733(1+2), 207-216.

179. R.Schulz, Laborpraxis 1996, 20(4), 42, 44, 46, 48.

180. S.Shahab A; W.Rashida M; D.Neil D, J.Chromatogr. A 1996, 737(2), 315-324.

Title	Analyte	Technique	Remarks/Comments	References
Magic angle spinning NMR techniques for the study of surfactants	Surfactants	NMR techniques	Technique is very useful for identification of molecules with restricted motions in solutions	181
Use of thin layer and high performance liquid chromatography for the study of the adsorption of surfactants on a river sediments	Surfactants	TLC and HPLC	The adsorption of tri butyl phenolethyleneoxide containing various lengths of ethylene phenol an a revering sediment was studied by TLC and HPLC	182
Spectrophotometric determination of inorganic substances; highly sensitive and chromogenic agents	Surfactants	Spectrophotometry	Surfactants mixed coordination compleses and by solid phase spectrophotometry	183

181. O. Hari; C. Kim, Bull Korean Chem. Soc., 1997, 18(3), 271-273.

182. T. Cserhati; V. Nemeth-Kiss; E. Forgacs, J. Biochem. Biophysics Methods, 1996, 33(2), 81-88.

183. K. Ohashi; H. Imura, Bunseki, 1997, (3), 215-223.

Title	Analyte	Technique	Remarks/Comments	References
Determination of surfactants in surface water critical review	Ionic and nonionic surfactants	Indirect tensametric techniques (ITT)	ITT and combined with Bias Sepn, scheme, useful in the analysis of nonionic surfactant and their metabolites are broadly described, levels of concentration of ionic and nonionic surfactant in surface water river water or treated sewage	184
Determination of CMC using wetting method	Surfactants	--	It is used for the rapid determination of CMC wetting isotherm of low energy polymer surfaces were obtained for e.g. solutions of micelle formation surfactants	185

184. Z. Lukaszewski, Chem., 1996, 50-51, 1-22.

185. V. D. Dolzhikova; G. Y. Bogdanova, Khim., 1997, 38(3), 196-198.

Title	Analyte	Technique	Remarks/Comments	References
Evaluation of CMC of surfactants through the UV SI bands of styrene	Surfactants	Ultra violet	The effect of surfactants on the UV spectrum of aqueous styrene solution was studied by considering the absorption ratios (Rpv) at peak and valley of the solvent induced (s-i) bands	186
Analysis of surfactants	Ionic and amphoteric nonionic surfactant	--	Analysis of surfactants	187
Analysis of surfactants by capillary electrophoresis/ mass spectrometry	Surfactants	Capillary electrophoresis/ mass spectrometry	Analysis of surfactants	188

186. W. Sopitkittiku; R. Wataneski; S. Watanesk, J. Sci. Soc., Thailand, 1997, 23(3), 253-258.

187. Igarashi; A. Matasutani; K. Yamada, Beinseki, 1997, (12), 999-1005.

188. Y.Janaka; Y.Kishimoto; K.Otsuka, Terabe Shingeru, 1997, 129.

Title	Analyte	Technique	Remarks/Comments	References
Some chromatographic determination of surfactants in cleaning surfaces	Surfactants	TLC, Super critical fluid chromatography (SFC) and HPLC	Separation of surfactant is done by TLC and quantified by SFC according to degree of ethoxylation and alkyl chain length. Retention time determined with HPLC	189
Simultaneous analytical method for surfactants	Surfactants	HPLC	14 surfactants [(C_8-C_{16} betaines) C_8 - C_{14} diethanolamides C_{12}-C_{16} acyl methyl tannries and C_{12}-C_{14} alkyl ethers] were identified in cosmetics and cleansing comopounds	190

189. J. Bohnen; B. Foellner; G. Rohm; H. Kruessmann, SOFW J., 1998, 124(11), 714, 716-719.

190. K.Masukawa; Tsujimura Ky[4], Jpn. Kokai Tokkyo Appl., 1997, 96/151-156.

Title	Analyte	Technique	Remarks/Comments	References
Trace analysis of surfactants using chromatographic and electrophoretic techniques	Surfactants ionic and neutral	Chromatographic, electrophoretic, HPLC and GC	Determination of linear alkyl benzene sulfonates in river water by HPLC and CE are discussed to show the capability of these methods for environmental analysis	191
Ternary surfactant mixtures in semi infinite geometry	Surfactants	Semi infinite geometry	Ternary surfactant mixtures	192
Role for surface active agent in drugs	Surfactants	--	Surface active agents in drugs	193

191. Vogt; K. Heinig, Fresenius J. Anal. Chem., 1999, 363(7), 612-618.

192. H. Tsuge, Kagaku to Kyoibu, 1999, 47(4), 228-231.

193. M. Tasinkevych; A. Ciach, J. Chem. Phys., 1999, 110(15), 7548-7455.

Title	Analyte	Technique	Remarks/Comments	References
Identification and quantification of anionic and nonionic surfactants in waste water by means of FIA-API-MS	Anionic and nonionic surfactant	Flow injection ionization (FIA) mass spectrometry (MS)	FIA-FPA-MS techniques is used for identification of surfactants	194
Suitability on quantitative analysis of cationic surfactants using JIS method	Cationic surfactants	JIS method	Quantitative analysis of surfactants	195

194. J. Efer; W.Engewald; V.Ceglarck; A. Schreiber, GIT Lab J., 1999, 3(3), 192, 194-196.

195. Z. S. Zhong; T.H.Q. Wu; Jingxi Huagong, 1999, 16, 127-129.

Title	Analyte	Technique	Remarks/Comments	References
Quantitative analysis of bio surfactants using Fourier transform infra red (FT-IR) spectroscopy	Bio surfactants	Fourier transform infra red (FT-IR)	Quantitative analysis of surfactants	196
Determination of nonyl phenol poly ethoxylates and their lipophilic metabolites in sewage effluents by normal phase high performance liquid chromatography and fluorescence	Surfactants	HPLC	Determination of surfactants and fluorescence detection	197
Determination of nonyl phenol ethoxylate surfactants in waste water	Surfactants	--	Determination of surfactant from waste water	198

196. J.Gartshore; Y.C. Lim; D.G. Cooper, Biotechnol. Lett. 2000, 22(2), 169-172.

197. M. Ahel; W.Giger; E.Molnar; S.Ibric, Craot. Chem. Acta 2000, 73(1), 209-227.

198. R-K Smith; M. Brown; J.Stowe, Am. Chem. Soc., Div. Environ. Chem. 2000, 40(1), 89-91.

Title	Analyte	Technique	Remarks/Comments	References
Spectrophotometric method for the determination of anionic surfactant chloroform content	Anionic surfactant	Spectrophotometric	Study was carried for determining the optimal methylene blue and chloroform doses	199
Development of a HPLC method for analysis of linear alkyl benzene sulphonates and detection of UV and FTIR spectroscopy using thermoscopy interface	Anionic surfactant	Reversed phase hiogh performance liquid chromatography UV and FTIR	Separating a mixture of linear Go-B. chromatograms pntained with UV and FTIR	200

199. H.Cao; Z.Wu-Yang; Z.Guo-Liang; L.Zhang; C.Zhi-ming; Z.Le-Liu; Y. Xu-Wei; Z.Ming-Zhu; Y.Liu; W.jan-Zheng, Jilin Daxue Ziran Kexue Xuebao 2000, (4), 88-90.

200. T.H.Jran; N.X. Nguyen; T.H.Tran, Tap Chi Hoa Hoc 1999, 37(3), 76-79

Title	Analyte	Technique	Remarks/Comments	References
Determination of cationic surfactants by capillary zone electrophoresis and micellar electrokinetic chromatography with deoxychlorate micelles in the presence of large organic concentrations	Cationic surfactants	Capillary zone electrophoresis and micellar electrokinetic chromatography	The procedure was applied to the determination of the surfactants in industrial and household formulation with excellent resolution between homologous detection limits of a few μgml^{-1} and reproducibilties between 2%	201
Determination of the structure of complexes formed by a cationic polymer and mixed anionic surfactants by small angle neutron scattering	Complexes by cationic polymer and mixed anionic surfactants	Small angle neutron scattering	Sodium alkanoates, NaOCl, NaDe, NaDod and mixtures of NaPal complexes formed by surfactants with cationic potato starch studied by small angle neutraon scattering (SANS)	202
Seperation method of an anionic surfactant from crude oil	Anionic surfactant	IR spectroscopy	A new, simple and rapid method was established to separate anionic surfactants which is used in increasing of oil recovery from oil crude oil containing anionic surfactants was eluted	203

201. M.A.Mottaleb, Springer-Verlag Interface 2000.

202. J.M.Herrero-Martinez; E.F.Simo-Alfonso; C.Mongay-Fernandez; G.Ramis-Ramos, J. Chromatogr., A 2000, 895(1+2), 227-235.

203. J.Merta; M.V.Garamus; I.A.Kuklin; R.Willumeit; P.Stenius, Langmuir 2000, 16(26), 10061-10068.

Title	Analyte	Technique	Remarks/Comments	References
Determination of nonyl phenolethoxylate oligomers by liquid chromatography electrospray mass spectrometry in river water and nonionic surfactants	Nonionic surfactants (nonyl phenol ethoxylates, NPE)	Liquid chromatography-electrospray, mass spectrometry	NPE oligomers separated on poly(vinyl alcpholic)gel column using acetonitrile -30mM NH_4Ac as the melting point followed by ESI-MS detection	204
Spectrophotometric studies about some dyes-anionic surfactant interactions in aqueous solutions	Nonionic surfactants	Spectrometric studies	Spectrometric studies about some dyes-anionic surfactant interactions in aqueous solutions and intensity of absorbance is observed	205
Solvent extraction-spectrofluorometric determination of anionic surfactants using acridine orange	Anionic surfactant	Solvent extraction-spectrofluorometric	Solvent extraction-spectrofluorometric determination of anionic surfactants using acridine orange	206

204. M.Takino; S.Daishima; K.Yamaguchi, J. Chromatogr., A 2000, 9041(1), 65-72.

205. E.Chirila; I.Carzeanue; S.Dobrinas, Talanta, 2000, 53(1), 271-275.

206. A.Pal; M.Bandyopadhyay, Indian J. Chem. Technol., 2000, 7, 105-108.

Title	Analyte	Technique	Remarks/Comments	References
Determination of anionic and amphoteric surfactants using LC/MS	Anionic and amphoteric surfactants	Liquid chromatography / mass spectrometry	This method is applicable for the determination of anionic and amphoteric surfactants individually in several shampoos	207
Determination of anionic surfactants in detergents by microporous membrane liquid extraction and flow injection spectrophotometry	Anionic	Liquid-liquid extraction and flow injection spectrophotometry	Determination of anionic surfactants in detergents by microporous membrane liquid extraction and flow injection spectrophotometry	208
Electrophotometry nuclear magnetic resonance studies of mixed anionic-nonionic surfactant micelles	Anionic-nonionic surfactant	Electrophoretic nuclear magnetic resonance (ENMR)	The electrophoretic mobilities of mixed micelles of binary surfactant mixture of anionic surfactant NA dodycyl sulfate (SDS) and sugar based nonionic dodecyl malone-bis-N methyl glucamide measured by ENMR	209

207. Y. Miyamae; K.Yoshizawa; J.Tsuchiya, Bunseki Kagaku 2001, 50(1), 61-67.

208. L.Jing Fu; J.gui-Bin, Microchem. J. 2001, 68(1), 29-33.

209. P.C.griffiths; E.Pettersson; P.stilbs; A.Y.F.Cheung; A.M.Howe; A.R.Pitt, Langmuir 2001, 17(22), 7178-7181.

Title	Analyte	Technique	Remarks/Comments	References
New method for surfactant quantification by HPLC-GPC	Surfactant	High performance liquid chromatography/ Gel permeation chromatography	New method for surfactant quantification by HPLC-GPC	210
Separation and determination of homologous of linear alkyl benzene sulfonates by non aqueous capillary zone electrophoresis using alkyl ammonium salts in ethanol	Surfactant	Capillary zone electrophoresis	Separation and determination of homologous of linear alkyl benzene sulfonates by non aqueous capillary zone electrophoresis using alkyl ammonium salts in ethanol	211
Fluorescence and X-ray diffraction studies on binding and complexes of surfactants and dansylated polyelectrolytes with sulfonates groups	Complexes of surfactants	Flourescence and X-ray diffraction method	CTAB on polyelectrolytes ADDan containing different amounts of sulfonates groups was studied by fluorescence spectrum of dansyl and complexe film of CTAB or DTAC (dodecyl trimethyl ammonium chloride) were obtained by precipitation and their fluorescence anisotropy	212

210. L.Lobmeyer, Houshold Pres. Prod. Ind. 2001, 38(3), 54-58.

211. J.M.Herrero-Martinez; F.E.Simo-Alfanso; G.Ramis-Ramos, Electrophoresis 2001, 22, 2017-2024.

212. B.Ren; Z.Tong; F.Gao; X.Liu; F.zong, Polymer 2001, 42(17), 7291-7298.

Title	Analyte	Technique	Remarks/Comments	References
Study on the determination of trace cetyl trimethyl ammonium based on the discoloration reaction of brilliant green	Cetyl trimethyl ammonium and cetyl pyridinium chloride	--	Study on the determination of trace cetyl trimethyl ammonium based on the discoloration reaction of brilliant green	213
Determination of Zwitterionic and cationic surfactants by High performance liquid chromatography with chemi-luminiscent nitrogen detection	Zwitterionic and cations	HPLC	The use of chemi-luminiscent nitrogen specific detection (CLND) combined with an HPLC separation allow for the identification and quantification of cations and zwitterionic surfactant	214
Qualitative determination of the trace anionic surfactant with visible spectrophotometry	Cationic surfactant	Spectrophotometry	Determination of trace anionic surfactant. The system contains bromocresol green as indicator, chloroform as oil phase and a mixed aqueous solution of anionic surfactant and Na_3PO_4-Na_2HPO_4 buffer as water phase	215

213. H.Ying-Ping; C.Ru-Xiu, Fenxi Kexve Xvebao 2001, 17(2), 97-101.

214. R.C.Harrison; A.C.Lucy, Journal of Chromatography A 2002, 956(1-2), 237-244.

215. F.Wang; X.Wang; Z.Cui, Riyong Huaxue Gongye 2002, 32(1), 65-67.

Title	Analyte	Technique	Remarks/Comments	References
Spectrophotometric determination of nonionic surfactants in water by using membrane filter	Nonionic surfactant (complex)	Spectrophotometric	Method using membrane filter was developed to determine polyoxyethylene nonionic surfactants. Method is based on the collection of nonionic surfactants from a water sample formation of nonionic surfactants ferric thiocyanate complex	216
Spectrophotometric study of interaction in the system sodium dodecyl sulfate-cetyl pyridinium chloride- methylene blue	Anionic and cationic	Spectrophotometric	Complexation of a cationic dye (methylene blue) with anionic and cationic surfactants was studied spectrophotometrically	217
Determination of CMC values of Tween20 with some synthetic dyes	Nonionic surfactant (synthetic dye)	Spectrophotometric	Determination of CMC values of Tween20 with some synthetic dyes	218

216. E.Nakamura; S.Mukai, Analytical Science 2001, 17, 947-948.

217. T.V.Vladimirova; E.E.Morgunova, Russian Journal of Applied Chemistry 2001, 74(12), 2095-2097.

218. H.K.Joshi; G.Desai; C.M.Desai; H.D.Joshi, Journal of the Institution of Chemists India 2001, 73(5), 180-181.

Title	Analyte	Technique	Remarks/Comments	References
Method and apparatus for determination of surfactant in water and their application for monitoring of octadecylamine	Surfactant	--	Method and apparatus for determination of surfactant in water and their application for monitoring of octadecylamine	219
Method for quantifiying surfactant	Nonionic surfactant	Colorimetric method	Quantity of surfactant (eg. Polysorbate, polyoxyethylene, polyoxypropylene glycol) in a sample containing actin protein	220
Determination of unsulfated matter in surfactants by Ion exchange chromatography	Surfactants	Ion exchange chromatography differential refractometer	Determination of compound in a sulfonated surfactants was determined with a set of ion exchange columns	221

219. S.I.Nefedkina, Teploenergetika 2002, (3), 54-58.

220. M.Kakuta; M.Janikown; N.Kuroyunagi, PCT Int. Appl., 2002.

221. M.Jian; C.Jian-Hua, Jingxi Huagang 2001, 18(8), 445-447.

Title	Analyte	Technique	Remarks/Comments	References
Determination of trace quaternary ammonium surfactants in water by combining solid phase extraction with surface assisted laser desorption/ionization spectrometry	Quaternary ammonium surfactants	Solid phase extraction with surface assisted laser desorption/ionization spectrometry	This study demonstrates the possibility of combining solid phase extraction with surface assisted laser desorption/ionization (SALDI) mass spectrometryto det	222
Extraction and seperation of cationic surfactants from river sediments; application to Spectrophotometric determination of cationic surfactant in an aquatic environment using membrane filters	Cationic surfactant	Spectrophotometric	The quantitative extraction of cationic surfactant in river water sediments was studied	223
Analysis of surfactants in formulation by mass spectrometry	Surfactants	Mass spectrometry	Coupling of electrospray ionization (ESI) mass spectrometric with a liquid chromatography for characterizing surfactant components in formulations offers a simple and inexpensive alternative	224

222. C.Yu-Chei; S.Mei-Chuan, Rapid Communication in Mass Spectrometry 2001, 15(24), 2521-2525.

223. S.Hui-Chie; H.Tetsuya; H.Noriko; K.Issei; T.Shigeru, Analytical Sciences 2001, 17, 1291-1294.

224. R.Spilker; B.Menzebach; K.Kube, Rivista Italiana Delle Sostanze Grasse 2001, 78(4), 241-246.

Title	Analyte	Technique	Remarks/Comments	References
Concentration on glass seperatory funnel wall of anionioc surfactants by ion association with methylene blue	Anionic surfactant	--	The method could be used to determine anionic surfactants in tap in river water samples	225
Spectrophotometric determination of trace ionic and nonionic surfactants based on a collection of a membrane filter as the ion associate of the surfactant with Erythrosine B	Ionic and nonionic surfactants	Spectrophotometric method	Method for the determination of trace surfactants with Erythrosine B (EB) based on the aqueous reaction and the collection on membrane filter by filtration	226
Spectrophotometric determination of nonionic surfactanta after removing of cationic surfactants by filteration with a membrane filter	Nonionic and cationic surfactants	Spectrophotometric method	Filtration with a membrane filter was studied to remove cationic surfactants which interfered with the Spectrophotometric determination of nonionic surfactants with thiocyanate iron (II) or thiocyanate cobalt (II)`	227

225. I.Sanemasa; E.Oota; K.Aoi; Z.Jin-Zi, Analytical Sciences 2002, 18(3), 347-350.

226. K.Yamamoto; M.Oka; H.Murakami, analytica Chimica Acta 2002, 455(1), 83-92.

227. S.Mukai; E.Nakamura, Bunseki Kayaku 2001, 50(10), 709-712.

Title	Analyte	Technique	Remarks/Comments	References
Analysis of anionic surfactants in environmental water samples by fluorometry with rhodamine B	Anionic surfactant	Spectrofluorometry	This method was successfully applied to the determination of anionic surfactants in environmental water samples	228
Application of membrane filters for Spectrophotometric determination of cationic sutfactants in river water and sediment	Cationic surfactants	Spectrophotometric determination with membrane filters	Spectrophotometric determination of cationic surfactants with two membrane filters	229

228. X.Zhi-Hai; Li Hui-Yun; U. Xin; Y.qi, Fexi Shiyanshi 2001, 20(5), 47-48.

229. S.Hui-feng; M.Takamori; N.Hata; I.Kasahara; S.Taguchi, Journal of AoAc International 2001, 84(6), 1781-1785.

Title	Analyte	Technique	Remarks / Comments	References
Spectrophotometric determination of trace amounts of surfactants with bromochlorophenol blue after pre concentration on a cellulose powder	Cationic surfactant	Spectrophotometry	A single method for the spectrophotometry determination of trace surfactants base on a pre concentration technique involving collection on a cellulose powder was developed	230
Determination of dialkyl dimethyl ammonium surfactants in sewage based on the formation of pre micellar aggregates	--	--	A method is described for the determination of dialkyl diammonium surfactants in sewage, based on the formation of pre micellar aggregates with SDS and using the dye coomassie brilliant blue G	231
Determination of cationic and nonionic surfactants using LC/MS	Cationic and nonionic surfactants	LC/MS	A method was developed that made it possible to detect cationic and nonionic surfactants individually in mixtures	232

230. K.Yamamota; K.Nakashima; K.Tadashi, Bunseki Kagaku 2002, 51(3), 175-180.

231. F. Merino; S.Rubio; D.B. Perez, Analyst, 2001, 126(12), 2230-2234.

232. Y.Miyamae; T.Matsumoto; K.Yoshizawa; J.Tsuchiya, Bunseki Kagaku, 2002, 51(10), 921-627.

Title	Analyte	Technique	Remarks / Comments	References
Determination of anionic surfactants in environmental waters by flow injection potentiometric analysis	Anionic surfactant	Flow injection potentiometry	An anionic surfactantselective electrode propared by coating graphite rod with PVC compound containing triheptyl dodecyl benzene sulfonates (THDA-DBS) was developed	233
Determination of cationic surfactants in water samples by their enhanced resonance light scattering with azoviolet	Cationic surfactants	--	A simple assay of cationic surfactants in water samples was developed based on the measurements of enhanced resonance light scattering (RLS)	234
Determination of cationic surfactant by laser thermal lens spectrometry	Cationic surfactants	Laser thermal lens spectrometry	A novel method for the determination of cationic surfactants by laser thermal lens spectrometry was developed	235

233. Y.Wang; S.Guan; D.Hao;D.Dan, Fenxi Huaxue, 2002, 30(12), 1455-1458.

234. X.C. Yang; F.Y.Li; C.Z. Huang, Analytical and bioanalytical Chemistry, 2002, 374(5), 868-872.

235. Y. HongTao; Y.Zhang; Y.yang, Chinese Chemical Letters, 2002, 13(11), 1107-1110.

Title	Analyte	Technique	Remarks / Comments	References
Measuring the content of anionic surfactants in water	Anionic surfactant	Spectrophotometry	Spectrophotometric method is described for determining the anionic surfactant in water with methylene blue	236
Determination of nonionic surfactants and their biotransformation by products adsorbed on alive activated sludge	Nonionic surfactant	--	A procedure was developed for the determination of non ionic surfactants adsorbed on particle of alive and dead activated sludge	237
Determination of nonionic surfactants as bismuth-active substrates (BIAS)	Nonionic surfactant	Spectrophotometry	Spectrophotometry measurement of Bismuth-EDTA complexes with nonionic surfactant	238

236. L.Ji-Gi; H.Xue-Gang; J.Zhuang, Shandong Huagong, 2003, 32(1), 33-35.

237. A.Szymanski; B.Wyrwas; Z.Lukoszewski, Water research, 2003, 37(2), 281-288.

238. J. Bindzar, Cistirenske Listy 2002, (6), vii-viii.

Title	Analyte	Technique	Remarks / Comments	References
Quantitative determination of cationic and non-ionic surfactant in aqueous solutions of their mixtures by capillary zone electrophoresis	Nonionic and cationic surfactant	Capillary zone electrophoresis	Quantitative determination of cationic and non-ionic surfactant in aqueous solutions of their mixtures by capillary zone electrophoresis	239
ESI-MS studies of polyether surfactants behavior in reversed phase HPLC systems	Polyether surfactants	Reversed phase HPLC electrospray ionization mass spectrometry (ESI-MS)	ESI-MS studies of polyether surfactants behavior in reversed phase HPLC systems	240
ESI-MS studies of polyether surfactants behavior in reversed phase HPLC systems	Surfactants	NMR	ESI-MS studies of polyether surfactants behavior in reversed phase HPLC systems	241

239. T.V.Kharitonora; A.V.Rudner; N.I.Ivanova, Colloid Joutnal, 2003, 65, 244-247.

240. J.Jhu; Z.Shi, International Journal of Mass Spectrometry, 2003, 226, 369-378.

241. H.W. Otto; J.D. Britten; K.C. Larive, Journal of Colloid and Interface Science, 2003, 261, 508-513.

Title	Analyte	Technique	Remarks / Comments	References
Determination of anionic surfactants in the water by spectrophotometry with methylene blue	Anionic surfactant	Spectrophotometry	Determination of anionic surfactants in the water by spectrophotometry with methylene blue	242
Spetrophotometric determination of CMC value of Triton-X 100	Nonionic surfactant	Spectrophotometry	Spetrophotometric determination of CMC value of Triton-X 100	243
Determination of complicated surfactant components using Fourier transform ion cyclotron resonance mass spectrometry	Surfactants	Fourier transform ion cyclotron resonance mass spectrometry	FT-ICR-MS was used for analysis of two kinds of complicated surfactant sample all compound were structural analysis of molecules and identification of unknown sample	244

242. L.Cui; H.Ma; J.Sun, Huaxue Fenxi Jiliang, 2003, 12(3), 31-32.

243. H.K. Joshi, Journal of Institution of Chemist, 2002, 74, 146-148.

244. S. Xiong; D.Pu;Xin Bin; G.Wong, Fenxi huaxue, 2003, 31, 429-432.

Title	Analyte	Technique	Remarks / Comments	References
Separation and analysis of alkyl benzene sulfonate surfactants by HPLC and HPCE	Anionic surfactant	HPLC and HPCE	Separation and analysis of alkyl benzene sulfonate surfactants by HPLC and HPCE	245
Simultaneous qualitative analysis of anionic , cationic and nonionic surfactants in water by electrospray ionization mass spectrometry with flow injection analysis	Ionic and nonionic surfactant	Electrospray ionization mass spectrometry with flow injection	Simultaneous qualitative analysis of anionic , cationic and nonionic surfactants in water by electrospray ionization mass spectrometry with flow injection analysis	246

245. X.Xiao; X.Liu; S.Jiang, Huaxue Jinzhan, 2003, 15(1), 41-46.

246. M. Barco; C.Planas; O.Palacios, Analytical Chemistry, 2003, 75(19), 5129-5136.

Title	Analyte	Technique	Remarks / Comments	References
Application of two phase potentiometric titration to determine the basic substance in anionic surfactants used in the motion picture industry	Anionic surfactants	Potentiometric titration	A method to detect the basic substance in a series of anionic surfactants having inorganic sulfo groups being used in cine photographic industry has been optimized	247
FTIR study of surfactants bonding to feft nanoparticles	Surfactants	FTIR	Fept nanoparticles coated with 2 nm thick films of surfactants were studied as candidates for magnetic recording media	248
Rapid determination of nonionic surfactants in synthetic liquid detergents	Nonionic surfactants	--	An express method for nonionic surfactant determination is described based on extraction of polyethylene glycol alkylphenyl ethers from aqueous solution by chloroform in the presence of glycerol and boric acid	249
Methods of separate determination of synthetic SAS	Ionic and nonionic surfactants	--	Modern physicochem methods of separation, determination of ionic and nonionic surfactants are reviewed	250

247. A.R.Garifzyanov; Z.A.Telnov; N.I.Saveleva; V.F.Torpova; G.K.budnikov, Diagostika Materialov, 2002, 68(11), 9-16.

248. N.Shukla; C.liu; P.Jones; W.Dieter, Journal of Magnetism and Magnetic Materials, 2003, 266(1-2), 178-184.

249. T.I.Akhmetova; D.F.Khaibrakhmanova; E.I.Galyamova, Diagnostika Materialov, 2002, 68(4), 21-22.

250. A.I.Kulapin; T.V.Arinushkina, Diagnostika Materialov, 2001, 67(11), 3-11.

Title	Analyte	Technique	Remarks / Comments	References
Surfactant/nonionic polymer interaction. A NMR diffusometry and NMR electrophoretic investigation	Surfactants	NMR diffusometry and NMR electrophoretic	The interaction between the nonionic polymer poly(ethylene oxide) of molecular weight 20,000 and surfactants has been investigated in aqueous solution at 25 ^{0}C	251
Determination of homologs of quaternary ammonium surfactants by capillary electrophoresis using indirect UV detection	Cationic surfactants	Capillary electrophoresis with indirect UV detection	This investigation describes the simultaneous separation of two major non-chromophoric quaternary ammonium surfactants by capillary electrophoresis using indirect UV detection	252
LC-MS-(MS) determination of oxidative degradation products of nonylphenol ethoxylate carboxylates and nonylphenols in water	Nonionic surfactants	LC-MS-(MS)	LC-MS-(MS) determination of oxidative degradation products of nonylphenol ethoxylate carbolates and nonylphenols in water	253
Analysis and fate of surfactants in sludge and sludge-amended soils	Surfactants	(LC-MS) and (GC-MS)	The focus is on the application of LC-MS and GC-MS, discussing various aspects of these two techniques including sample preparation	254

251. E.Petterson; D.Topgaard; P.Stilbs; O.Soedermann, Langmuir, 2004, 20(4), 1138-1143.

252. L.Hsuch-ying; D.Wang-Hson, Journal of Chromatogr. A, 2004, 1025(2), 303-312.

253. M.Petrovic; P.Gehringer; H.Eschweiker; D.Barcelo, Water Science Technology, 2004, 50(5), 227-234.

254. M.Petrovic; D.Barcelo, Trends in analutical Chemistry , 2004, 23(10-11), 762-771.

Title	Analyte	Technique	Remarks / Comments	References
Analysis and characterization of surfactants by matrix assisted laser desorption/ionization time of flight mass spectrometry	Surfactants	MALDI-TOF-MS	A method for analysis and characterization of surfactants using MALDI-TOF-MS was developed	255
Capillary electrophoresis enhanced by automatic two-way background correction using cubic smoothing splines and multivariate data analysis applied to the characterization of surfactants	Surfactants	Capillary electrophoresis	Mixtures of the surfactant classes coconut diethanol amide, cocamidoperbetaine and alkylbenzene sulfonate were separated by capillary electrophoresis in several media containing organic solvents and anionic solvophobic agents	256
Fluorescence quenching method for the determination of sodium dodecyl sulfate with near infra red hydrophobic dye in the presence of Triton-X100	SDS	Fluorophotometric method	A fluorophotometric method for the determination of anionic surfactants SDS was proposed	257

255. Z.GuO; Z.Qing-Chun; L.Quan-Zhou; Z.Han-Fu, Fenxi Kexue Xuebao, 2002, 18(3), 182-185.

256. V.Bernabe-Zafon; J.R.Torres-Lapasio; S.Ortega-Gadea; E.F.Simo-Alfanso; G.Ramis-Ramos, Journal of Chromatogr., A, 2005, 1065(2), 301-313.

257. C.Zhu; H.Zheng; D.Li; S.Li; J.Xu, Spectrochimica Acta, Part A : Molecular and Biomolecular Spectroscopy, 2004, 60A(13), 3173-3179.

Title	Analyte	Technique	Remarks / Comments	References
Increasing UV detection sensitivity in the super critical fluid chromatographic analysis of alcohol polyethers	Alcohol polyethers	Supercritical fluid chromatography (SFC)	Derivatized samples were analysed bySFC coupled with both electrospray ionization mass spectrometry and UV absorbance detection	258
Analysis of surfactants in water environment by LC/MS	Surfactants	LC/MS	A review on LC/MS determination of surfactants in environmental water	259
Determination of anionic surfactants in tap water by HPLC-UV detection after solid phase extraction	Anionic surfactants	SPE, HPLC-UV	A catridge type solid phase extraction method for the determination of anionic surfactants, followed by HPLC-UV is described	260
Liquid chromatography mass spectrometry of nonionic surfactants using electrospray ionization	Nonionic surfactants	LC.MS using electrospray ionization	The analysis of nonionic surfactants was investigated by reversed phase liquid chromatography with mass spectrometry detection	261

258. B.J.Hoffman; L.T.Taylor; S.Riombelow; J.D.Pinkston, Journal of Chromatogr. A, 2004, 1052(1-2), 161-166.

259. A.Tanabe; K.Kawata, Zenku Kankyoken Kaishi, 2003, 28(4), 240-244.

260. H.Kitami; T.Watanabe; T.Kitahar; Y.Ishihara; J. Takano, Bunseki Kagaku, 2004, 53(8), 857-861.

261. Z.Jingke, Journal of Surfactants and Detergents, 2004, 7(4), 421-423.

Title	Analyte	Technique	Remarks / Comments	References
Analysis of neutral surfactants by non aqueous capillary electrophoresis using an electro osmotic flow reversal	Nonionic surfactants	Non aqueous capillary electrophoresis	The separation of KMZO. That infact a mixture of nonionic surfactants, was carried out by non aqueous capillary electrophoresis	262
Liquid chromatography mass spectrometry of nonionic surfactants using electrospray ionization	Nonionic surfactants	LC/MS using electrospray ionization	The analysis of nonionic surfactants was investigated by reversed phase liquid chromatography with mass spectrometry detection	263
Separate detection of homologous surfactants by means of solid contact unmodified and modified with molecular sieves potentiometric sensors	Surfactants	Potentiometric sensors	To improve the selectivity of surfactant sensor, the surface of their membranes was modified with molecula sieves with predetermined pore size	264

262. A.M.Desbene; L.Geulin; C.J.Morin; P.L.Desbene, Journal of Chromatogr, A, 2005, 1068(1), 159-167.

263. Z.Jingeke, Journal of Surfactants and Detergents, 2004, 7(4), 421-423.

264. A.T.Kulapin, R.K.Chernova; E.G.Kulapina; N.M.Mikhalova, Talanta, 2005, 66(3), 619-626.

Title	Analyte	Technique	Remarks / Comments	References
Liquid chromatographymass spectrometry hyphenation for exhaustive and unambiguous characterization of polyoxyethylene surfactants	Polyoxyethylene surfactants	LC/MS	Liquid chromatography mass spectrometry hyphenation for exhaustive and unambiguous characterization of polyoxyethylene surfactants	265
HPLC-NMR of fatty alcohol ethoylates	Fatty alcohol ethoylates	HPLC-NMR	The application of HPLC-NMR for the analysis of a mixture fatty alcohol ethoxylates (FAEs) is described	266

265. G.Cheguillaume; W.Buchmann; B.Desmazieres, J.Tortajade, Chromatographia 2004, 60(9/11), 561-566.

266. Magnetic Resonanace in Chemistry, 2005, 43(9), 729-735.

References :

[1] F.F. Runge, "Der Biddimgstriebder Stoffe" Verenschlaulicht in Selbstaqndiggewachsenen Bedern. Sebsterlag Oranenberg, Germany (1855).

[2] F. Goppelsroeder, Verk Naturforsch, Ces. Basel. 1861, 3, 268.

[3] C.F. Schonbein, Verk, Naturforsch. Ces. Basel, 1861, 3, 249.

[4] E. Fischer and E. Schmidner. Annalen, 1892, 272, 156.

[5] L. Reed, Proc.Chem. Soc., 1893, 9, 123.

[6] D.T. Day,Amer. Phil. Soc., 1897, 36, 112.

[7] M.S. Tswett. Ber. Deut. Boatan. Ges, 1906, 24, 235.

[8] R. KuhnandE.Lederer, Ser., 1931, 64, 1349.

[9] R. Kuhn, A. Winterstein and E. Lederer, Hoppe-Seyler's Z. Physiol.Chem., 1931, 197, 141.

[10] A.J.P. Martin and R.L.M. Synge. Biochem. J. 1941, 35, 91.

[11] A.J.P. Martin and R.L.M. Synze. Biochem. J., 1941, 35, 1358.

[12] M.W. Beyerink and R.L.M. Synge, Biochem. J., 1941, 35, 1358.

[13] H.P. Wijsman, D. De Beshouwdals, Mengsel Van. Mattase en Dentrinase Amsterdam 1898.

[14] N.A. Izmailov and M.S. Schraiber. Farmatsiya (Sotla), 1938, 3, 1.

[15] C. Lapp and Erali, Bull. Sci., Pharmacol, 1940, 47, 49.

[16] J.E. Meinhard and N.F. Hall. Anal. Chem., 1949, 21, 185.

[17] H. Jork, W. Funk and H. Wimmer, Physical and Chemical Detection Methods: Fundamentals, Reagents I; Thin-Layer Chromatography Reagents

and Detection Methods, Vol. la; VCH Verlagesgesellschaft: Weinheim, FRG, 1990, p. 464.

[18] N. Fatima and A. Mohammad, Sepn. Sci. TehnoL, 1984, 19, 429.

[19] A. Mohammad and N. Fatima. Chromatographia, 1986, 22, 109.

[20] A. Mohammad and S. Tiwari, Microchem. , J., 1991, 44, 39.

[21] N.V.K. Nanda and Y.P. Devi. J. Assoc. Offic. Anal. Chem., 1981, 64,729.

[22] J. Maslowaska and Z, Mlodzikowski, Chem. Anal., 1986, 31, 193.

[23] H.J. Issaq and E.W. Barr. Anal Chem., 1977, 49, 189.

[24] For an example of one of GAF corp's early acts promoting their trademarked surfactants, see Bus, Week, 1950, March 11, P. 42.

[25] C.E. Stevens in Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, New York, 2nd Edn., Vol. 19. p. 507.

[26] M. Abe, Curr. Opin Colloid Interface Sci., 1994, 4, 354.

[27] M.E. Hayes, E. Nestass and K.R. Hrebenar, CHEMTECH, 1986, 16, 239.

[28] S. Lang, Curr. Opin. Colloid Interface Sci., 2002, 7, 12.

[29] F.M. Menger and C.A. Littau,J.Am. Chem. Soc. 1991, 113,1451.

[30] F.M. Menger and C.A. Littau, J. Am. Chem.Sci. 1993, 115, 10083.

[31] W.M. Linfield, W.M. Linfield (ed): Anionic Surfactants. Marcel Dekker, NewYork, 1967.

[32] E.H.Lucassen- Reynders: Anionic surfactants – Physical chemistry of surfactant Action, Marcel Dekker, New York,1981

[33] B.R. Buestein, C.L. Hiliton: Amphotesic surfactants, Marcel Dekkar, New York, 1982.

[34] J.B.M. Hendry and A.J. Hockings Analyst. 1986, 111, P. 1431.

[35] ASTM D5079-90, American Society for Testing and Materials, West Conshohocken, PA.

[36] S.R. Epton, Trans. Faraday Soc., 1948,44, 226.

[37] S.R. Epton, Nature, 1947, 160, 795.

[38] J. Glazer and T.D. Smith, nature, 1952, 169, 497.

[39] V.W. Reid, G.F. Longman and E. Heinerth, Tenside surfactants Deterg. 1967, 4, 292.

[40] L.L. Schramm, R.G. Smith and J.A. Stone, Aostra J. Res. 1584, 1,5.

[41] T.M. Schmitt, Analysis of Surfactants, Dekker, New York, 2nd edn., 2001.

[42] Introduction to surfactant Analysis, ed. D.C. Cullum, Blackie, London, 1994.

[43] B.J. Birch and D.E. Clarke, Anal. Chim. Acta 1973, 67, 387.

[44] K. Vytras, Mikrochim. Acta (Wien), 1984,

[45] H.H.Y. Oei and D.C. Toro, J. Soc. Cormet, Chem. 1991, 42. 309.

[46] C.A. De Caro, Riv. Ital. Sostanze Grasse 1998, LXXV, 197.

[47] J. Gransveld and M.J. Faber, Tenside Surfactants Detrog., 1990, 27, 231.

[48] ASTM D2357-74, American Society for Testing and Materials, West Conshohocken, PA.

[49] D.O. Hummel, (Ed), Analysis of surfactants: Atlas of FTIR spectra with Interpretations, (1995). Hanser/Gardner: Cincinnati, OH.

[50] D.R. Brezinski (Ed.), An Infrared spectroscopy Atlas for the coatings Industry (1991), Federation of societies for coatings technology, Blue Bell, PA.

[51] G. Carminati, F. Caralli and F.Buosi, J. Am. oil Chem. Soc., (1998), 65, P. 699.

[52] H. Koenig, Tenside, (1974), 8, P. 63

[53] D.C. Cullum, Introduction to surfactant analysis, 1994, Blackie Academic and professional, Glasgow G642 NZ, UK.

[54] S. Laurier L, S. Elaine N, and D. Gerrael Marangoni, Annu. Rep. Prog. Chem., Sect.C, 2003, 99, 3-48.

[55] L. J. Cline Love et al., Anal. Chem. 56, 1132 A (1984).

[56] H. Hoffmann, G. Ebert, Angew. Chem. 100, 933 (1988).

[57] W.L. Ninze, Ann. Chim (Paris), 1987, 77, 167.

[58] D.W. Armstrong and M. McNeely, Anal. Lett., 1979 vol. 12, P. 1285.

[59] D.W. Armstrong; K.H. Bui and R.M. Barry, J. Chem. Educ., 1984, Vol. 61, No. 5, P. 457.

[60] O. Armstrong; R.Q. Terril, Anal. Chem., 1979, Vol. 51, No. 13, P. 2160.

[61] D.W. Armstrong, J. Liq. Chromatogr. 1980, Vol. 3, No. 6, P. 895.

[62] D.W. Armstrong and K.H. Bui, J. Liq. Chromatogr., 1982, Vol. 5, No. 6, P. 1043.

[63] J. Sherma, B.P. Sleekman and D.W. Armstrong, J. Liq. Chramatogr., 1983, 6(1), 95.

[64] D.W. Armstrong and J.Y. Stine, J. Am. Chem. Soc., 1983, 105 (10), 2962.

[65] D.G. Tabor and A.L. Underwood, J. Chromatogr., 1989,463 (1), 73.

[66] E.G. Sumina, E.V. Ermolaeva, N.V. Tyurina and N. Shtyko ZaVod. Lab., 2001, 67(5), 5

[67] Z. Mao andQ. Zhang, Fenxi Huaxue, 1984, 12(5), 455; Cited by R Zh Khim, 1984, 21 G442.

[68] S.N. Shtykov; E.G. Sumina E.V. Parshina and S.S. Lopukhova, Zh. Anal Khim., 1995, 50(7), 747.

[69] S.N. Shtykov; E.G. Sumina; E.V. Smushkina and N.V. Tyunna, J. Planar Chromatogr. 1999, 12(2), 125.

[70] A.Mohammad and V.Agarwal, J. Planar Chromatogr., 2000, 13(3), 210.

[71] A.Mohammad and Y.H. Sirwal, J. Planan Chromatogr., 2002, 15, 107.

[72] S .N. Shtykov; E.G. Sumina, Zh. Anal. Khim., 1998, 53(5), 508.

[73] S.N. Shtykov, E.G. Sumina and N.V. Tyurina, J. Planan Chromatogr., 2000, 113(4), 264.

[74] E.G.Sumina, E.V. Smushkina; S.N. Shtykov and N.V. Tyurina, Zavod.Lab., 2001,67(10), 13.

[75] E.G. Sumina; S.N. Shtykov and N.V. Tyurina, Izv. Vyesh-Uchebn. Zared., Khim.Khim Tekhmol., 2001, 44(4), 10

[76] S.N. Shtykov; E.V. Parshina; E.G. Sumina; I.V. Barabanova and M.I. Malova, RF Patent 20038593, Byull. Izobret., 1995, 18.

[77] E.G. Sumina, I.N. Ufimtseva and S.S. Lopukhova proc. 8th Russian-Japan Joint, Symp. On Analytical chemistry (RJSAC ' 96), Moscow, Saratov, 1996, 164.

[78] T.B. Nielsen; J.A. Reynolds, Metho US Enzymol. 1978, 48, 3.

[79] Helenius, K. Simons, Proc. Natl. Acad. Sci. 1977, 74, 529.

[80] P.G. Righatti, Isoelectric Focusing, Elsevier, Amsterdam 1983

[81] Electrophoresis (O.J. Bjerrum; B.J. Redola, eds.), 1987, 9.

[82] J.P. Andersen et al., Biochemistry 1986, 25, 6439.

[83] G.W. Welling, J. Chrominatogr. 1987, 418, 223.

[84] Ion-pair Chromatography (M.T. Hearn, ed.), M. Dekker, New York1985.

[85] High Performance Liquid chromatography in Biochemistry (A. Henscheri et. al., eds.), Verlag Chemie, Weinheim 1985.

[86] J.L. Torres et al., Anal. Biochem. 1988, 171, 411.

[87] J.F. Pankow and J.A. Cherry, Dense Chlorinated solvents, Waterloo Press, Postland, DR, 1996.

[88] D.M. Mackay and J.A. Cherry, Environ. Sci. Technol., 1989, 23, 630.

[89] Surfactant–Enhanced Subsurface Remediation, Emerging Technologies, ed. D.A. Sabatini, R.C. Knox and J.H. Harwell, American Chemical Society, Washington, DC, 1995,

[90] V. Dwarkanath and G.A. Pope, in Surfactants, Fundamentals and Applications in the Petroleum Industry, ed. L.L. Scheramm, Cambridge University Press, Cambridge, UK, 2000, P. 433.

[91] J.C. Fountain; A. Klimek; M.G. Beikirch and T.M. Middleton, J. Haz. Mater. 1991, 28, 295.

[92] C.N. Mulligan, R.N. Yong and B.F. Gibbs, Eng. Geol. 2001, 60, 371.

[93] Forms, Fundamentals and Applications in the petroleum Industry, ed. L.L. Schramm, American Chemical Society, Washington, DC, 1994.

[94] T.P. Lockhart and E. Borgarello, Prog. Colloid Polym. Sci., 1998, 109, 49.

[95] A.J. McCabe, D.T. Wilcox; B.A. Holm and P.L. Glick, J. Pediatr. Surg., 2000, 35, 1987.

[96] S. Kallapur and M.D. Ikegami, Amer. J. Perinatol., 2000. 17, 335.

[97] H. Hamm. C. Kroegel and J. Hohlfeld, J. Respir. Mech., 1996, 90, 251.

[98] M. Knoche, Weed Res., 1994, 34, 221.

Chapter - 2

Silica Thin-Layer Chromatographic Separation of Cetylpyridinium Chloride (CPC) from Polyoxyethylene (20) Sorbitan Monolaurate (Tween-20)

2.1 INTRODUCTION:

Surfactants as amphipathic compounds have been used in a variety of fields, such as the chemical, pharmaceutical and food industries, hospitals, homes and environments for cleaning, emulsification, solubilization and moisturizing [1]. Surfactant mixtures are used in various industrial processes, such as the creation of synthetic detergents, drug design, waste water purification, oil production etc. [2-4]. The cationic and nonionic surfactants are considered to influence the biological and chemical processes. For example, cationic surfactants including quaternary ammonium compounds have antimicrobial activity [1,5]. They have been known to disrupt cell membranes [6], interrupt protein functions [7], release intracellular K^+ and other constituents [8-9] and induce cell autolysis [10-11], on the otherhand, nonionic surfactants have the properties of increasing the penetration of hydrocortisone through skin [12], enhancing the fluorescence of metals chelates [13], preventing the adsorption of bacteria to hydrophobic surfaces [14-15] and interacting with phospholipids [16]. The biological activity of nonionic surfactants depends on the physico-chemical character of the hydrophobic moiety as well as on the number of hydrophilic ethylene oxide groups [17-18].

Numerous chemical and physico-chemical methods for the qualitative and quantitative determination of surfactants have been developed, the most wide spread among them are microbial sensor [19], amperometric biosensors [20], ion-pair formation with in-situ flow injection analysis utilizing dynamic surface tension detection [21], ion-selective electrode [22], ion-pairing chromatography with suppressed conductivity detection [23], spectrophotometric determination [24-31], capillary electrophoresis [32, 33], solid-phase extraction with surface assisted laser desorption/ionization spectrometry [34], electrospray ionization mass spectrometry with flow injection analysis [35], liquid chromatography/atmospheric pressure ionization mass spectrometry [36], Flow Injection analysis-Atomic Pressure ionization-Mass Spectrometry (FIA-API-MS) [37]. All these methods need sophisticated instruments and expertise. The conventional techniques of surfactant detection, which are mainly based on chromatography, need

expensive instrumentation. Thus, elaborating simple, rapid and selective method for surfactant determination is still a challenge to the chemists. Thus, here a simple and quick TLC method is reported for cationic and nonionic surfactants. The proposed methods capable to determine surfactant contents in both individual and mixed solutions. It does not involve the use of toxic chemicals. We have successfully separated CPC (cationic surfactant) from nonionic surfactants including Tween-20. The mutual separation of CPC and Tween-20 is important because of their wide applicability in many environmental benign systems [38-41].

2.2 Experimental:

All experiments were performed at 30 ± 50C.

Apparatus:

A TLC applicator was used for coating silica gel on 20 x 3.5 cm glass plates, the chromatography was performed in 24 x 6 cm glass jars. A glass sprayer was used to spray reagent on the plate to locate the position of the spot of analyte.

Chemicals and reagents:

Silica gel G (Merck, India), alumina, kieselguhr (CDH, India), sodium chloride, methanol and tetrahydrofuran (THF, 0.89 KgL^{-1}, Merck, India) were used. All the chemicals were analytical reagent grade.

Surfactants studied:

Triton-X (Tx-100), Brij-35 (Bj-35), Tween-20 (Tw-20), Cween-20 (Cw-20), Cween-40 (Cw-40), Cween-60 (Cw-60), Cetylpyridiniumchloride (CPC), Cetyltrimethylammonium bromide (CTAB), Tetradecyltrimethylammonium bromide (TTAB), Hexadecyltrimethylammonium chloride (HDTAC) and Dodecyl trimethylammonium bromide (DTAB).

Test solutions:

Solutions of the surfactants were prepared by dissolving appropriate weights in methanol to give concentrations of 1% (1g/100ml).

Detection Reagent:

Modified dragendorff reagent prepared as described below was used to detect all the surfactants.

Dragendorff reagent comprised two solutions A and B. Solution A was prepared from the two solutions:

I. Solution of bismuth subnitrate ($BiONO_3.H_2O$, 1.7 g) dissolved in acetic acid (20 ml) and diluted 100 ml with water.

II. Solution of potassium iodide (65g in 200 ml water).

Both solutions were transferred into 1L flask and acetic acid (200 ml) was added. The contents were diluted to one litre with water (solution A).

Solution B was prepared by dissolving barium chloride dehydrate ($BaCl_2.2H_2O$, 89:290 g) in 1 L water.

Solution A and b were mixed in 2:1 v/v, ratio and used.

The following stationary and mobile phases were used.

(i) Stationary phase:

Code No.	Stationary Phase
S_1	Silica Gel G
S_2	Alumina
S_3	Kieselguhr

(ii) Mobile Phase:

Code No.	One component system
M_1	Double Distilled Water (DDW)
M_2	THF
M_3	Tap Water
M_4	Saline water

Code No.	Two component system	Code No.	Two component system
M_5	THF + DDW 1 : 9	M_{12}	THF + DDW 8 : 2
M_6	THF + DDW 2 : 8	M_{13}	THF + DDW 9 : 1
M_7	THF + DDW 3 ; 7	M_{14}	THF + Tap Water 6 : 4
M_8	THF + DDW 4 : 6	M_{15}	THF + Saline Water 6 : 4
M_9	THF + DDW 5 : 5		
M_{10}	THF + DDW 6 : 4		
M_{11}	THF + DDW 7 : 3		

Preparation of TLC plates:

TLC plates were prepared by mixing silica gel G with double distilled water in 1: 3 ratio. The resultant slurry was mechanically shaken for 5 min and then it was coated onto glass plates with the help of a TLC applicator to give a layer of 0.25 mm thickness. The plates were first air dried at room temperature and then activated by heating at 100^0C for 1 h. After activation, the plates were kept in air tight chamber until used.

Procedure:

The surfactant solutions (0.01ml) were spotted on TLC plates with micropipette. The spots were dried at room temperature (30^0C). The glass jars containing mobile phase were covered with lids and left for 10 min for saturation before introducing the plates for development. The plates were developed with chosen solvent system by ascending technique. The solvent ascent was fixed at 10 cm in all cases. After development, the plates were

detected by using Dragendroff reagent. The development time was 25-30 min for 10 cm ascent.

For separation of mixture, equal volumes of surfactants were mixed and 0.01 ml of the resultant mixture was applied on TLC plate (S_1). The plate was developed with M_{10}, the spots were detected and R_F values of the spots of these surfactants were calculated.

In order to examine the nature of water on the mobility of surfactants, the distilled water in M_{10} was substituted with tap or saline water and resultant mobile systems M_{14} (THF + Tap Water, 6:4) and M_{15} (THF + Saline water, 6:4) were used as eluents.

For the study of effect of nature of adsorbent layers, such as, silica gel G, alumina and kieselguhr on the mobility of different surfactants, a comparison has been performed by developing the chromatograms of these surfactants in M10.

For the separation of microgram quantity of Tween20 from milligram quantities of CPC, TLC plates were first spotted with 0.01 ml of Tween20 (100 μg). After complete drying of spot, a series of 0.01 ml of CPC containing (0.1 - 0.77 mg) was spotted on the same spot of TLC plate. Similarly, for the separation of microgram quantity of CPC from milligram quantities of Tween-20, TLC plate was first spotted with 0.01 ml of CPC (100 μg) solution and then with 0.01 ml of the standard solutions containing (0.1 – 1.0 mg) of Tween20 on the same TLC plate. The spots were dried and these plates were developed with M10. The separated spots were visualized and R_F values were calculated.

To study the effect of presence of metal cations as impurities on the separation of surfactants, 0.01 ml each of standard test solutions of surfactants (CPC and Tween20) was spotted on TLC plates (S_1) followed by spotting of 0.01 ml of the cations being considered as impurities. The plates were developed with M10, detected and R_F values of the separated surfactants were calculated.

The limits of detection of different amounts of CPC and Tween20 were determined by spotting different surfactants on the TLC plates, developing the plates and detecting the corresponding spots. The method was repeated with successive lowering of the amount of CPC and Tween-20 until

no spot was detected. The minimum amount of detectable on the TLC plate was taken as the limit of detection.

For semi-quantitative determination by spot-area measurement method, 0.01 ml of a series of various standard solutions (1-5%) of CPC was spotted on silica gel layers. The plates were developed with M10. After detection, the spots were copied onto tracing paper from the chromatoplates and then area of each spot was calculated.

2.3 Results and Discussion:

Results are depicted in Tables and Figures. In all fifteen mobile phases used for the chromatography of surfactants. In single component systems (DDW, tap water and saline water) almost all the surfactants stay at the point of application. However, with THF, all surfactants appeared as badly tailed spots (R_L - $R_T \geq 0.3$) HDTAC is the exception which gave well formed compact spot near the point of application ($R_F = 0.11$).

In case of two component solvent systems (THF + water, in different volume ratio M_5 – M_{13}) surfactants show differential migration. The results are presented in Table 2.1. From the data of Table 2.1, it is evident, that at the lower concentration of THF (upto 30%) almost all the cationic surfactants except DTAB remained at the point of application and all nonionic surfactants except Triton-X 100 appeared as tailed spot (R_L - $R_T \geq 0.3$). Most of the surfactants (cationic and nonionic) produced compact spots with mobile phase systems containing 40 – 70% THF (M_8 – M_{11}) and hence this concentration range of THF is useful for the separation of cationic surfactants from nonionics.

The low mobility of cationic surfactants may be attributed to their strong electrostatical attraction with negative silinol groups on silica gel surface. While, in case of nonionic surfactants, they may adsorb on silica surface via hydrogen bonding [42, 43].

The plot of R_F vs. mole fraction (Figure 2.1) shows that the best separation of CPC from Tween-20 is achieved with mobile phase containing 0.06 mole fraction of THF (or 0.94 mole fraction of water). Therefore, M_{10} (THF + DDW, 6:4) was selected for detailed study.

The results showing the influence on the mobility of different surfactants on substitution of DDW in M_{10} with tap water (M_{14}) or saline water (M_{15}) are documented in Table 2.2. Both cationic and nonionic surfactants show slightly higher mobility in tap water-THF system compare to their mobility in DDW-THF. This increase in mobility may be due to the presence of certain dissolved salts in tap water. The hardness of tap water as determined by EDTA titration method was found to be 320 ppm. Thus, tap water contains bicarbonates, sulfates and chlorides of calcium and magnesium in addition to other dissolved salts. In case of saline water (3.5% NaCl) – THF all cationic surfactants compared to their mobility in DDW or tap water-THF system show higher mobility. It is due to the fact that electrolyte for (e.g. NaCl) in eluent causes a decrease in the adsorption of ionic surfactants on the surface of adsorbent [44].

The effect of nature of different adsorbents (viz. silica gel, alumina and kieselguhr) on the mobility of surfactants was examined using M_{10} as eluent and the results are presented in Figure 2.2. From 2.2, following trends are noticeable,

1. The mobility of all surfactants decreases in the following order of selected adsorbents;
   Alumina > Kieselguhr > Silica Gel
2. Cationic surfactants can not be separated from nonionic surfactants on alumina layer as all surfactants migrate with the mobile phase.
3. Poor separation of cationic surfactants from nonionic surfactants is possible on Kieselguhr layer.
4. Best separation of each cationic surfactant from all nonionic surfactants is possible on silica layer.
5. The separation efficiency pattern of adsorbent is
   Silica Gel > Kieselguhr > Alumina

It was observed that 100 µg of each Tween-20 and CPC can be easily separated from 0.7 mg of CPC and 1.0 mg of Tween-20 respectively. Thus, proposed TLC system is capable to separate microgram quantities of cationic surfactants from milligram quantities of nonionic surfactants and vice versa.

The results showing the effect of various metal cations as impurities on the separation efficiency of CPC from Tween-20 are presented in Figure

2.3. it is clear from this Figure that separation of CPC from Tween-20 is hampered in the presence of Co^{2+}, Uo_2^{2+} and Al^{3+} due to co migration of both surfactants in the presence of these cations. No other metal cations influenced on separation.

The lowest possible concentration limit detected after successive dilution was 3 μg/0.01 ml of both CPC and Tween-20. This amount was taken as the lowest detectable concentration limit, which indicates that the proposed TLC method is highly sensitive for the detection of cationic and nonionic surfactants.

In addition to qualitative analysis, quantitative evaluation of surfactants is often required. We have attempted semi-quantitative determination of surfactants by the measurement of the spot-area. A linear relationship was obtained for CPC when the spotted amount of the sample (100-500 μg) was plotted against the area of the spot (Figure 2.4). It follows the empirical equation $\zeta^2 = km$, ζ is the area of the spot, m is the amount of the solute and k is the constant. At higher concentration, a negative deviation from linear law was observed.

2.4 Application:

To widen the applicability of proposed method, the separation of CPC from Tween-20 was carried out from a variety water samples. The results presented in Tables 2.3 show that the CPC and Tween-20 can be easily identified in a variety of water samples of water samples after their mutual separation on S_1 layer developed with M_{10}.

Table 2.1 R_F value of different surfactants with different mobile phase using silica gel as a stationary phase.

	One component system				Two component system THF + Water								
	M_1 DDW	M_2 THF	M_3 Tap water	M_4 Saline water	M_5 1 : 9	M_6 2 : 8	M_7 3 : 7	M_8 4 : 6	M_9 5 : 5	M_{10} 6 : 4	M_{11} 7 : 3	M_{12} 8 : 2	M_{13} 9 : 1
Triton-X 100	0.00	0.45T	0.03	0.00	0.15T	0.42	0.58	0.72	0.76	0.87	0.87	0.88	0.84
Brij-35	0.00	0.43T	0.00	0.00	0.36T	0.61T	0.57T	0.77	0.80	0.81	0.85T	0.68T	0.30T
Tween20	0.00	0.45T	0.00	0.00	0.12	0.40T	0.65T	0.76	0.80	0.86	0.82	0.75T	0.32T
Cween20	0.00	0.5T	0.04	0.00	0.32T	0.40T	0.40T	0.57T	0.67T	0.77T	0.79T	0.77T	0.50T
Cween40	0.00	0.45T	0.00	0.00	0.31T	0.40T	0.41T	0.42T	0.60T	0.77T	0.68T	0.65T	0.50T
Cween60	0.00	0.23T	0.00	0.00	0.12	0.37T	0.60T	0.72	0.81	0.81	0.81	0.81	0.30
CPC	0.00	0.20T	0.00	0.00	0.00	0.00	0.03	0.05	0.06	0.07	0.10	0.12	0.07
CTAB	0.00	0.45T	0.00	0.00	0.00	0.00	0.03	0.05	0.08	0.07	0.12	0.14	0.08
TTAB	0.00	0.12T	0.03	0.00	0.00	0.00	0.05	0.05	0.07	0.12	0.10	0.11	0.08
HDTAC	0.00	0.11	0.03	0.00	0.00	0.00	0.05	0.05	0.12	0.11	0.17	0.16	0.10
DTAB	0.00	0.25T	0.09	0.06	0.07	0.07	0.12	0.06	0.08	0.08	0.12	0.12	0.10

(T = tailed spot, $R_L - R_T \geq 0.3$)

Table 2.2 Effect of nature of water on the mobility of surfactants chromatographed on S_1 layer.

	6 : 4 THF + DDW M_{10}	**6 : 4 THF + Tap water M_{14}**	**6 : 4 THF +Saline water M_{15}**
Triton-X 100	0.87	0.88	0.81
Brij-35	0.81	0.86	0.82
Tween20	0.86	0.89	0.80T
Cween20	0.77T	0.79	0.80T
Cween40	0.77T	0.82	0.74T
Cween60	0.81	0.82	0.70T
CPC	0.07	0.14	0.60
CTAB	0.07	0.13	0.72
TTAB	0.12	0.13	0.64
HDTAC	0.11	0.13	0.58
DTAB	0.08	0.11	0.53

Table 2.3 Identification and separation of CPC and Tween-20 in different water samples.

	CPC	**Tween-20**
DDW	0.14	0.89
Tap Water	0.20	0.88
Saline Water	0.21	0.81
River Water	0.15	0.87

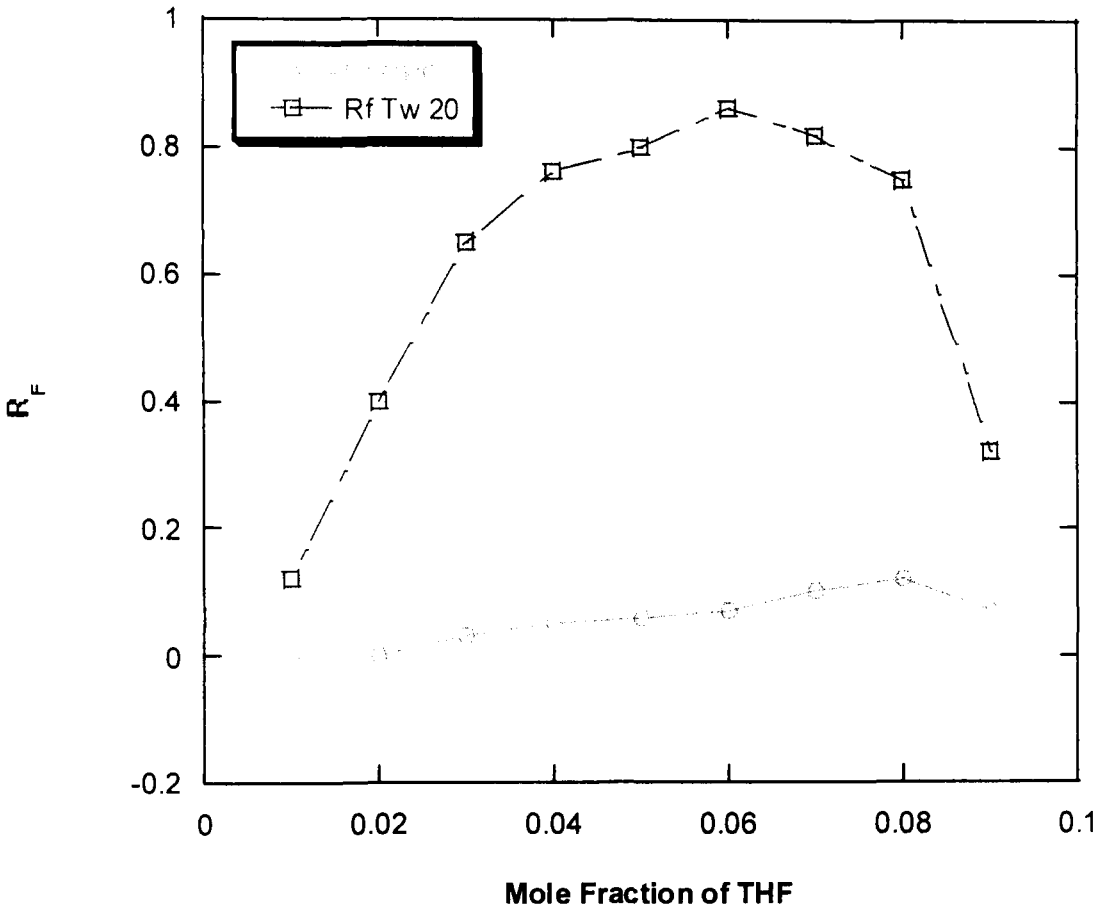


Figure 2.1 Plot of R_F vs. Mole Fraction of THF for mutual separation of CPC from Tween-20

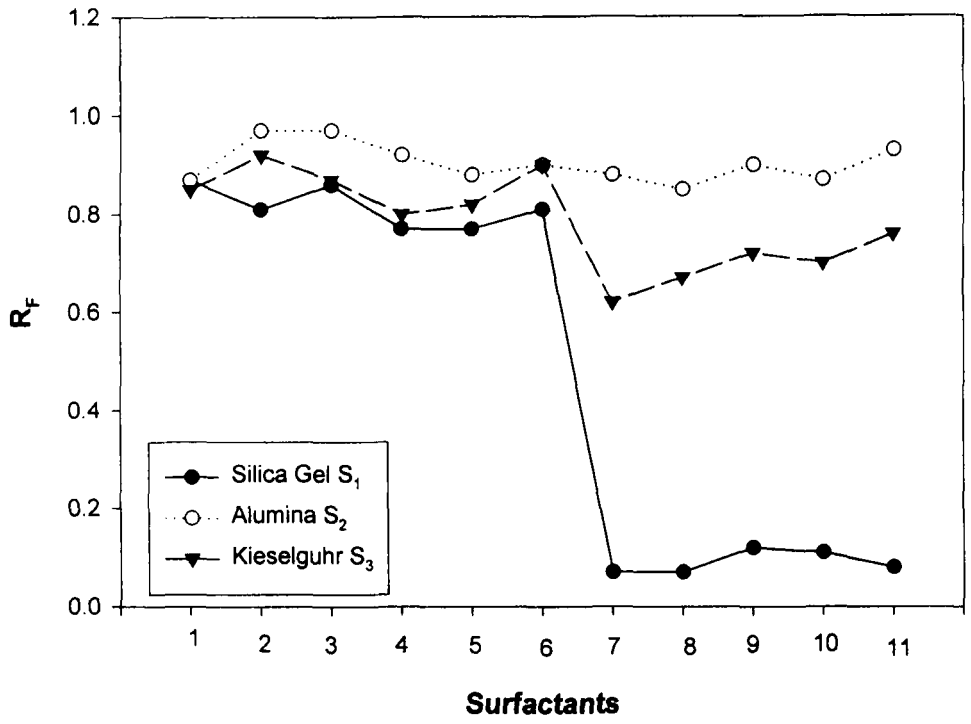


Figure. 2.2 Effect of nature of Silica Gel (S_1), alumina (S_2) and Kieselguhr (S_3) on the mobility of different surfactants using M_{10} as eluent.

1. Triton-X100, 2. Brij-35, 3. Tween-20, 4. Cween-20, 5. Cween-40, 6. Cween-60, 7. CPC, 8. CTAB, 9. TTAB, 10. HDTAC and 11. DTAB

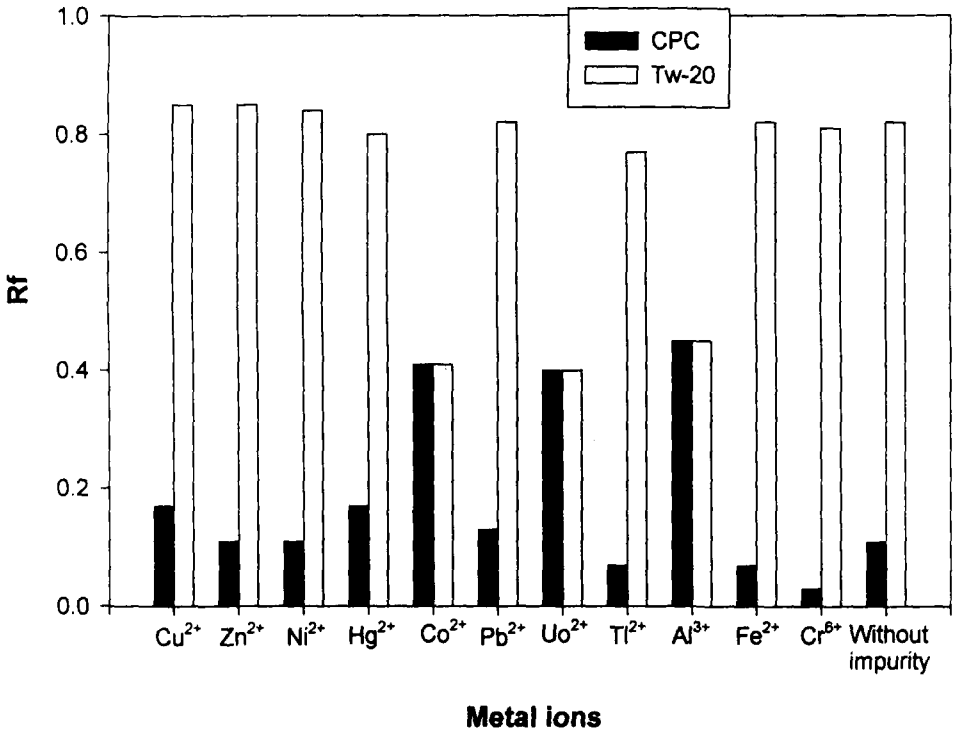


Figure 2.3 Separation of CPC from Tween-20 on Silica layers in the presence of metal cation as impurities with M_{10}

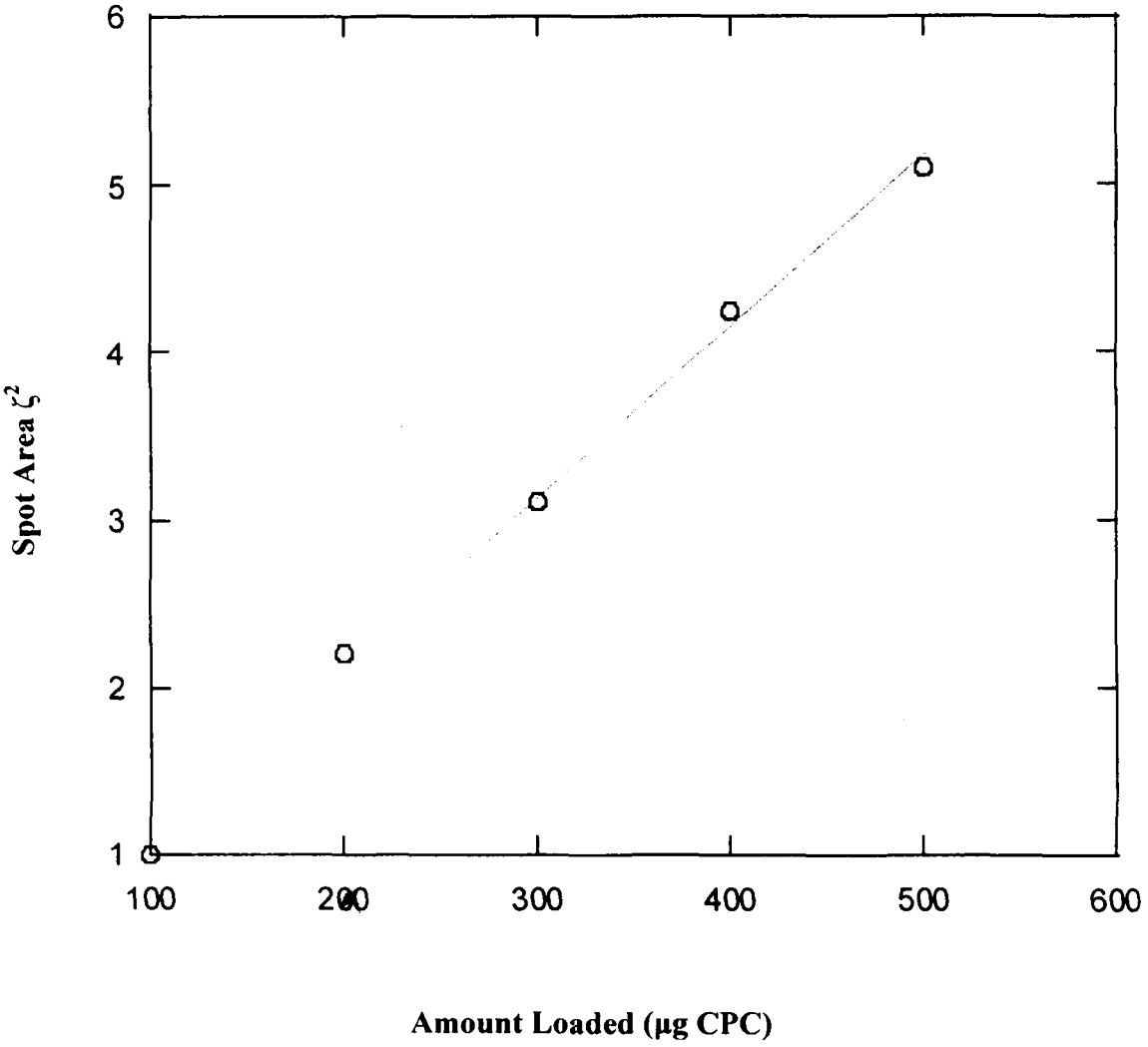


Figure 2.4 Calibration curve for Semi-Quantitative determination of CPC

Referenes :

[1] A.M. Schwartz and J.W. Perry (1979) Surface Active Agents: their chemistry and technology. Ed. A.M. Schwartz and J.W. Perry, Huntington: Krieger.

[2] M.J. Rosen, Phenomena in mixed surfactant systems, J.F. Scamehorn, Ed., ACS Symp. Ser. 31, Washington, DC: J. Am. Chem. Soc., 1986, p.144.

[3] H.F. Eicke; W. Meier and H. Hammerich, Colloids Surface A: Physicochem. Eng. Aspects, 1996, 118, 141.

[4] Sh. G. Dixit, A.R. Mahadeshwar and S.K. haram, Colloids Surf. A: physicochem. Eng. Aspects, 1998, 133, 69.

[5] W.B. Hugo and A.D. Russel, factors influencing the efficacy of antimicrobial agents. In principles and practice of Disinfection, preservation and sterilization. 2nd Edn. Ed. A.D. Russel, W.B. Hugo and G.A. J. Ayliffe 1992, pp. 90-92 Oxford: Blackwell. Scientific publications.

[6] T.G. Scharff and W.C. Maupin, Correlationof metabolic effects of benzal konium chloride with its membrane effects in yeast. Biochemical pharmacology 1960, 5, 79-86.

[7] F.W. Putnam, Advances in Protein Chemistry, 1948, 4, 79-122.

[8] Y. Sakagami; H. Yokoyama; H. Nishimura; Y. Ose and T. Tashima, Applied and Environmental Microbiology 1989, 55, 2036-2040.

[9] J.P. Cabral, Journal of Basic Microbiolgy 1993, 33, 219-225.

[10] H.-Y. Cho; T. Tsuchido; H. Ono and M. Takano, Journal of Fermentation and Bioengineering 1990, 70, 11-14.

[11] T. Tsuchido; A. Svarachern; H. Soga an M. Takano, Antimicrobial Agents and chemotherapy 1990, 34, 781-785.

[12] P.P. Sarpotdar and J.L. Latz, Drug, Dev. Ind. Pharm., 1986, 12, 1625.

[13] A.Sanz-Medel; R.F. de la Campa and J.I.G.Alonso, Analyst, 1987, 112, 493.

[14] M. Humphries; J. F. Jaworzyn and J.B. Cantwell FEMS Microbiol. Ecol., 1986, 38, 299.

[15] M. Humphries; J. F. Jaworzyn and J.B. Cantwell and A. Eakin, FEMS Microbiol. Lett. 1987, 42, 91.

[16] T. Inoue; K. Miyakawa and R. Shimozawa, Chem. Phys. Lipids, 1986, 42, 261.

[17] M. Djimbo and A.J. Moes, J. Pharm. Bdg., 1986, 41, 393.

[18] J.C. Blake-Haskins, D. Scala, C.D. Rhein and C.R. Robbins, J. Soc. Cosmet. Chem., 1986, 37, 199.

[19] Y. Nomura; K. Ikebukuro; K. Yokoyama; T. Takeuchi; Y. Arikawa, S. Ohno and I. Karube, Anal Lett. 1994, 27, 3095.

[20] A.N.Reshetilov; I.N.Semenchuk; P.V.Iliasov and L.A.Taranova, Anal.Chim. Acta, 1997, 19, 347.

[21] T.E.Young and R.E.Synovec, Talanta, 1996, 43, 889.

[22] S.Alegret; J.Alonso; J.Bartroli; J.Baro-Roma; J.Sanchez and M.Delvalle, Analyst, 1994, 119, 2319.

[23] M.Y.Ye; R.G.Walkup and K.D.Hill, J.Liq.Chromatogr., 1994, 17, 4087.

[24] E.Nakamura and S.Mukai, Analytical Sciences 2001, 17, 947-948.

[25] T.V.Vladimirova and E.E.Morgunova, Russian Journal of Applied Chemistry, 2001, 74(12), 2095-2097.

[26] S.Hui-Feng; T. Nase; M.Takamori; N.Hata; I.Kasahara and S.Taguchi, Analytical Sciences, 2001, 17(11), 1291-1294.

[27] S.Hui-Feng; M.Takamori; N.Hata; I.Kasahara and S.Taguchi, Journal of AoAc International, 2001, 84(6), 1781-1785.

[28] K.Yammamoto; M.Oka and H.Murakami, Analytica Chimica Acta 2002, 455(1), 83-92.

[29] S.Mukai and E.Nakamura, Bunseki Kagaku 2001, 50(10), 709-712.

[30] K.Yammanoto; K.Nakashima and T.Kimura, Bunseki Kagaku 2002, 51(3), 175-180.

[31] Z.Shu-Lin; L.Shu-Ting and B.Tan, Fenxi Kexne Xuebao 2003, 19(3), 240-242.

[32] C.Vogt, GIT Labor-Fachzeits Chrit 2003, 47(5), 551-555.

[33] L.Hsuch-Ying and D.Wang-Hsion, J. Chromatogr. A 2004, 1025(2), 303-312.

[34] C.Yu-Chei and S.Mei-Chuan, Rapid Communications in Mass Spectrometry 2001, 15(24), 2221-2225.

[35] M.Petrovic and D.Barcelo Journal of Mass Spectrometry 2001, 36(11), 1173-1185.

[36] M.Barco; C.Planus; O.Palacios; F.Ventura; J.Rivera and J.Caixach, Analytical Chemistry 2003, 75(19), 5129-5130.

[37] J.Efer; W.Engewald; V.Ceglarck and A.Schrieber, GIT Lab. J. 1999, 3(3), 192, 194-196.

[38] C.Qing-Xi; H.Huang and K.Isao, Journal of Protein Chemistry, 2003, 22(5), 481-487.

[39] K.Lim and A.mustapha, Journal of Food Protein-ion, 2004, 67(2), 310-315.

[40] M.Singh; V.S.Gill; H.Thippareddi; R.K.Phebus; J.L.Marsden; T.J. Herald and A.L.Nutsch, Foodborne Pathogens and Disease, 2003, 2(3), 233-241.

[41] W.R.Jennifer and K.A.Kinney, J. Environ. Engrg., 2004, 130(3), 292-299.

[42] H.Rupprecht and H.Liebl, Kolloid Z.Z. Polym. 1972, 250, 719.

[43] J.R.Aston; D.N.Furlong; F.Grieser; P.J.Scales and G.G.Warr, in Adsorption at the Gas/Solid and Liquid/Solid Interface, J.Rouquerol and K.S.W. Sing (Ed.) Elsevier, Amsterdam, 1982, pp 97-102.

[44] Surfactants and Interface Phenomenon, 3rd Ed., Milton J. Rosen, John Wiley and Sons, Inc, 2004, p 53.